Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Palladium-Catalyzed Direct C–H Allylation of Arenes without Directing Groups

Cheng-Hao Ying and Wei-Liang Duan*

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

E-mail: wlduan@mail.sioc.ac.cn

Supporting Information

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General Methods

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under nitrogen. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Varian instrument (400 MHz, 100 MHz and 376 MHz, respectively). ^{1}H, ^{13}C NMR chemical shifts are reported vs tetramethylsilane signal or residual protio solvent signals.

Arenes were distilled over sodium benzophenone ketyl or CaH_2 under nitrogen.

Ligands (**4**,[1a] **5**,[1b] **6**,[1a] **7**,[1a] **8**,[1c] and **10**[1d]) were synthesized following the literature procedures. All other chemicals and solvents were purchased from commercial company and used as received.

Experimental Details and Characterization Data

I. General Experimental Procedure for Table 1.

$Pd(OAc)_2$ (4.5 mg, 0.02 mmol), additive (0.1-0.2 mmol), ligand (0.02 mmol), allylic acetate (0.20 mmol), 4Å molecular sieve (20 mg) and benzene (1 mL) were added to a solution tube and the resulting solution was heated to 120 ^{o}C and reacted for 15 hours. After cooling to room temperature, the mixture was filtrated through a pad of silica gel with ethyl acetate and concentrated under vacuum. The yield was detected by ^{1}H NMR with CH_2Br_2 as the internal standard.

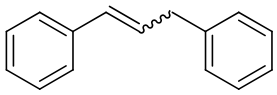
II. General Experimental Procedure for Table 2.

$Pd(OAc)_2$ (4.5 mg, 0.02 mmol), Ag_2CO_3 (0.0275 mg, 0.10 mmol), ligand **4** (3.9 mg, 0.02 mmol), allylic acetate (0.20 mmol), 4Å molecular sieve (20 mg) and benzene (1 mL) were added to a solution tube and the resulting solution was heated to 120 ^{o}C and reacted for 15 hours. After cooling to room temperature, the mixture was filtrated through a pad of silica gel and washed with ethyl acetate. The filtrate was

concentrated under vacuum, and the residue was purified by silica gel flash column chromatography to afford the Z/E-products.

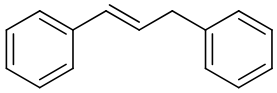
III. General Expermential Procedure for Table 3.

$Pd(OAc)_2$ (4.5 mg, 0.02 mmol), Ag_2CO_3 (0.0275 mg, 0.10 mmol), ligand **4** (3.9 mg, 0.02 mmol), allylic acetate (0.20 mmol), 4Å molecular sieve (20 mg) and arene (1 mL) were added to a solution tube and the resulting solution was heated to 120 ^oC and reacted for 15 hours. After cooling to room temperature, the mixture was filtrated through a pad of silica gel and washed with ethyl acetate. The filtrate was concentrated under vacuum, and the residue was purified by silica gel flash column chromatography to afford the Z/E-products.



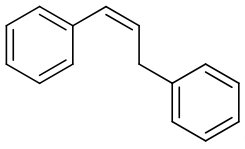
3aa

^1H NMR spectral data of the isolated products matched the spectral data of known compounds reported in the literatures.[2,3]



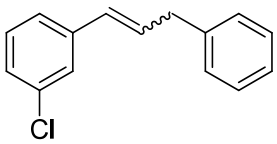
(E)-**3aa**

(E)-1,3-diphenylpropene (CAS: 3412-44-0)[2]



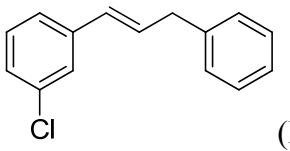
(Z)-**3aa**

(Z)-1,3-diphenylpropene (CAS: 1138-83-6)[3]



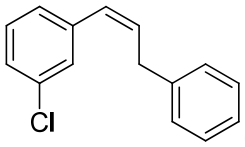
3ca

^1H NMR spectral data of the isolated products matched the spectral data of known compounds reported in the literatures. [4,5]



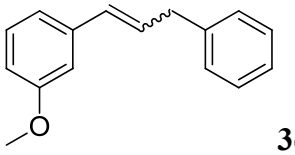
(E)-**3ca**

(E)-1-(3-chlorophenyl)-3-phenylpropene (CAS: 132931-76-1)[4]



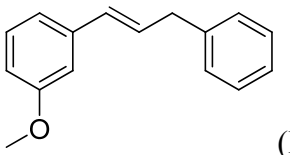
(Z)-**3ca**

(Z)-1-(3-chlorophenyl)-3-phenylpropene (CAS: 132931-77-2)[5]



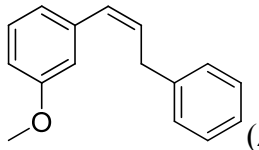
3da

^{1}H NMR spectral data of the isolated products matched the spectral data of known compounds reported in the literatures. [6]



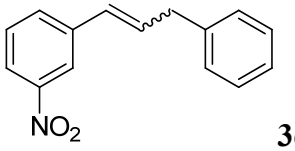
(E)-**3da**

(E)-1-(3-methoxyphenyl)-3-phenylpropene (CAS: 870620-86-3)[6]



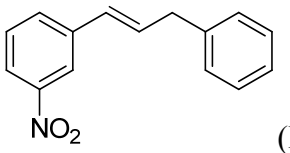
(Z)-**3da**

(Z)-1-(3-methoxyphenyl)-3-phenylpropene (CAS: 1392095-73-6)[6]



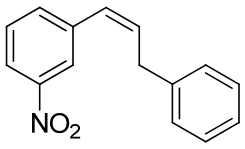
3ea

^{1}H NMR spectral data of the isolated products matched the spectral data of known compounds reported in the literatures.[7]



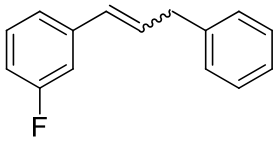
(E)-**3ea**

(E)-1-(3-nitrophenyl)-3-phenylpropene(CAS:1372720-65-4)[7]



(Z)-**3ea**

(Z)-1-(3-nitrophenyl)-3-phenylpropene(CAS:1372720-59-6)[7]



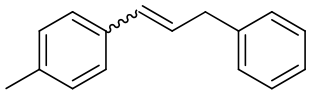
3fa

1-(3-fluorophenyl)-3-phenylpropene

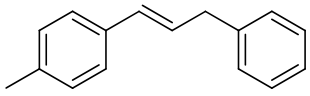
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.29 (m, 2H), 7.25-7.20 (m, 3H), 7.11-7.01 (m, 1H), 6.97-6.87 (m, 1H), 6.54 (d, J = 11.6 Hz, 0.36H), 6.44-6.33 (m, 1.2H), 5.90 (dt, J_1 = 11.6 Hz, J_2 = 7.2 Hz, 0.36H), 3.66-3.62 (m, 1H), 3.66 (d, J = 7.6 Hz, 0.74H), 3.55 (d, J = 5.6 Hz, 1.2H).

HRMS (EI) calcd for $C_{15}H_{13}F$ $(M)^+$: 212.1001, found: 212.1003.

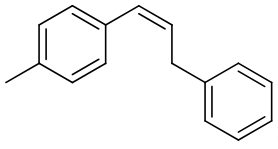
GC-MS: m/z: 212 $(M)^+$; E isomer: 75.01% (area), Z isomer: 24.99% (area).


3ga

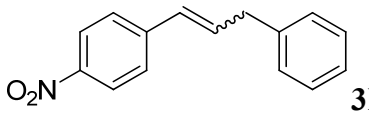
^{1}H NMR spectral data of the isolated products matched the spectral data of known compounds reported in the literatures. [2,8]


(E)-**3ga**

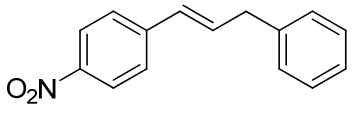
(E)-1-(4-methylphenyl)-3-phenylpropene (CAS: 134539-87-0)[2]


(Z)-**3ga**

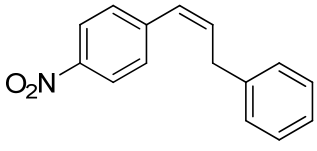
(Z)-1-(4-methylphenyl)-3-phenylpropene (CAS: 227187-00-0)[8]


3ha

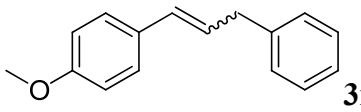
^{1}H NMR spectral data of the isolated products matched the spectral data of known compounds reported in the literatures.[9]


(E)-**3ha**

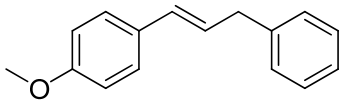
(E)-1-(4-nitrophenyl)-3-phenylpropene (CAS: 156904-24-4)[9]


(Z)-**3ha**

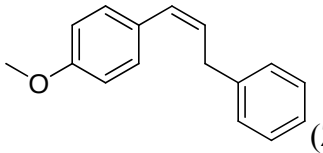
(Z)-1-(4-nitrophenyl)-3-phenylpropene (CAS: 183621-36-5)[9]


3ia

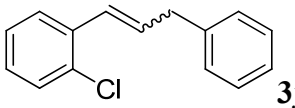
^{1}H NMR spectral data of the isolated products matched the spectral data of known compounds reported in the literatures.[3,9]


(E)-**3ia**

(E)-1-(4-methoxylphenyl)-3-phenylpropene (CAS: 35856-81-6)[3]


(Z)-**3ia**

(E)-1-(4-methoxylphenyl)-3-phenylpropene (CAS: 183621-24-1)[9]

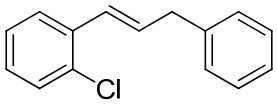

3ja

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 7.6 Hz, 0.65H), 7.42-7.13 (m, 8H), 6.86 (d, J = 15.6 Hz, 0.52H), 6.67 (d, J = 11.6 Hz, 0.36H), 6.32 (dt, J_1 = 15.6 Hz, J_2 = 7.2 Hz, 0.55H), 5.99 (dt, J_1 = 11.6 Hz, J_2 = 7.2 Hz, 0.38H), 3.59 (d, J = 7.2 Hz, 1.15H), 3.54 (d, J = 7.2 Hz, 0.84H).

HRMS (EI) calc. for $C_{15}H_{13}Cl$ $(M)^+$: 228.0706, found: 228.0704.

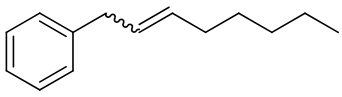
GC-MS: m/z: 228 $(M)^+$; E isomer: 53.13% (area), Z isomer: 46.87% (area).

^{1}H NMR spectral data of the E-product matched the spectral data of the known compound reported in the literatures.[4]



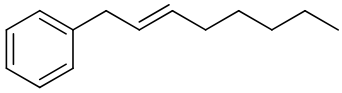
(E)-**3ja**

(E)-1-(2-Chlorophenyl)-3-phenylpropene (CAS: 1191300-42-1)[4]



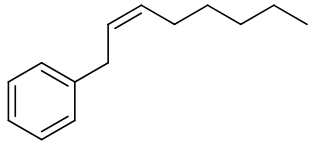
3ka

^{1}H NMR spectral data of the isolated products matched the spectral data of known compounds reported in the literatures.[10,11]



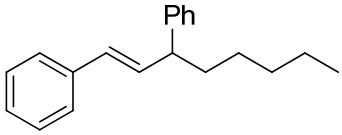
(E)-**3ka**

(E)-1-phenyl-2-octene (CAS: 42079-83-4) [10]



(Z)-**3ka**

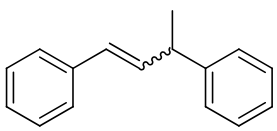
(Z)-1-phenyl-2-octene (CAS: 372193-70-9)[11a]



3ka′

(E)-1,3-Diphenyl-1-octene (CAS: 157670-40-1)[11b]

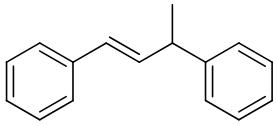
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.11 (m, 10H), 6.40 (d, J = 16.0 Hz, 1H), 6.33 (d, J_1 = 16.0 Hz, J_2 = 7.2 Hz, 1H), 3.40 (q, J = 7.2 Hz, 1H), 1.79 (q, J = 7.6 Hz, 2H), 1.42-1.19 (m, 6H), 0.87 (t, J = 6.4 Hz, 3H).



3la

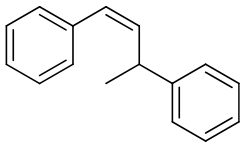
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.17 (m, 10H), 6.48 (d, *J* = 16.0 Hz, 0.15H), 6.40-6.39 (m, 1.7H), 5.83 (t, *J* = 10.4 Hz, 0.17H), 4.04-3.98 (m, 0.18H), 3.66-3.62 (m, 0.85H), 1.46 (d, *J* = 9.2 Hz, 2.55H), 1.39 (d, *J* = 9.2 Hz, 0.45H).

^{1}H NMR spectral data of the isolated products matched the spectral data of known compounds reported in the literatures.[12, 13]



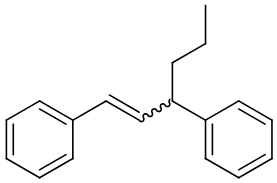
(E)-**3la**

(E)-1,3-diphenyl-1-butene (CAS: 7302-01-4)[12]



(Z)-**3la**

(Z)-1,3-diphenyl-1-butene (CAS: 7302-00-3)[13]



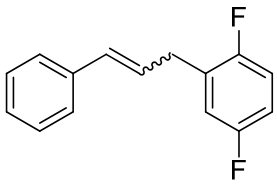
3ma

1,3-diphenyl-1-hexene

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.20 (m, 10H), 6.52 (d, *J* = 11.6 Hz, 0.45H), 6.43-6.31 (m, 2H), 5.86 (t, *J* = 11.2 Hz, 0.46H), 3.85-3.76 (m, 0.48H), 3.46-3.92 (m, 1H), 1.83-1.64 (m, 2H), 1.40-1.29 (m, 2H), 0.934 (t, *J* = 7.2 Hz, 2H), 0.835 (t, *J* = 6.8 Hz, 1H).

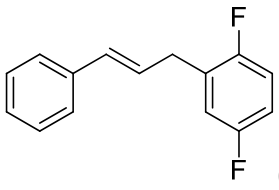
HRMS (EI) calc. for $C_{18}H_{20}$ $(M)^+$: 236.1565, found: 236.1570.

GC-MS: m/z: 236 $(M)^+$; E-isomer: 65.98% (area), Z-isomer 34.02% (area).



3ab

Two isomers were separated by silica gel column chromatography.

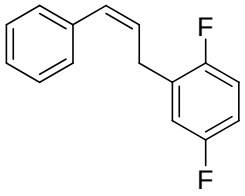


(E)-**3ab**

(E)-1-phenyl-3-(2,5-difluorophenyl)propene

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.35 (m, 2H), 7.28 (t, J = 8.0 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 7.01-6.93 (m, 2H), 6.90-6.85 (m, 1H), 6.47 (d, J = 15.6 Hz, 1H), 6.29 (dt, J_1 = 16.0 Hz, J_2 = 6.8 Hz, 1H), 3.54 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8 (dd, J_{CF} = 241.3 and 2.3 Hz), 157.0 (dd, J_{CF} = 241.2 and 3.0 Hz), 137.2, 132.3, 129.0 (dd, J_{CF} = 19.1 and 7.6 Hz), 128.7, 127.5, 126.7, 126.3, 117.0 (dd, J_{CF} = 23.7 and 5.3 Hz), 116.3 (dd, J_{CF} = 25.2 and 9.1 Hz), 114.3 (dd, J_{CF} = 24.4 and 8.4 Hz), 32.3 (d, J_{CF} = 3.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -119.4, -124.6.

HRMS calc. for $C_{15}H_{12}F_2$ $(M)^+$: 230.0907, found: 230.0911.

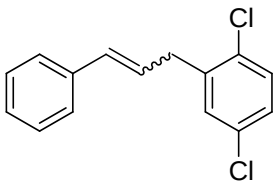


(Z)-**3ab**

(Z)-1-phenyl-3-(2,5-difluorophenyl)propene

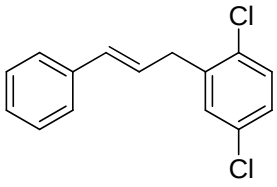
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.34 (m, 2H), 7.30-7.25 (m, 3H), 7.00-6.84 (m, 3H), 6.66 (d, J = 11.2 Hz, 1H), 5.78 (dt, J_1 = 11.2 Hz, J_2 = 7.6 Hz, 1H), 3.65 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9 (dd, J_{CF} = 241.9 and 2.6 Hz), 157.0 (dd, J_{CF} = 241.6 and 3.3 Hz), 136.9, 131.5, 129.5 (dd, J_{CF} = 18.3 and 7.4 Hz), 128.8, 128.5, 128.2 (d, J_{CF} = 1.2 Hz), 127.2, 116.6 (dd, J_{CF} = 23.9 and 4.9 Hz), 116.2 (dd, J_{CF} = 25.0 and 8.6 Hz), 114.1 (dd, J_{CF} = 24.3 and 8.6 Hz), 27.7 (dd, J_{CF} = 2.6 and 1.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -129.3, -124.2.

HRMS calc. for $C_{15}H_{12}F_2$ $(M)^+$: 230.0907, found: 230.0906.



3ac

Two isomers were separated by silica gel column chromatography.

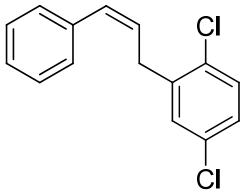


(E)-**3ac**

(E)-1-phenyl-3-(2,5-dichlorophenyl)propene

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.36 (m, 2H), 7.32-7.31 (m, 2H), 7.29 (s, 1H), 7.27-7.20 (m, 2H), 7.16-7.140 (m, 1H), 6.47 (d, J = 16.0 Hz, 1H), 6.30 (dt, J_1 = 16.0 Hz, J_2 = 6.8 Hz, 1H), 3.62 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.6, 137.0, 132.4, 132.3, 130.5, 10.3, 128.6, 127.7, 127.4, 126.2,126.1, 36.9.

HRMS (EI) calc. for $C_{15}H_{12}Cl_2$ $(M)^+$: 262. 0316, found: 262. 0318.

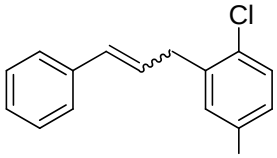


(Z)-**3ac**

(E)-1-phenyl-3-(2,5-dichlorophenyl)propene

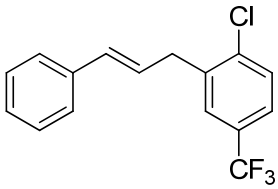
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.34 (m, 2H), 7.30-7.24 (m, 5H), 7.16-7.13 (m, 1H), 6.68 (d, J = 11.2 Hz, 1H), 5.77 (dt, J_1 = 11.6 Hz, J_2 = 7.2 Hz, 1H), 3.72 (d, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8, 132.6, 132.3, 131.6, 130.4, 129.7, 128.6, 128.3, 127.8, 127.6, 127.1, 32.2.

HRMS (EI) calc. for $C_{15}H_{12}Cl_2$ $(M)^+$: 262. 0316, found: 262. 0313.



3ad

Two isomers were separated by silica gel column chromatography.

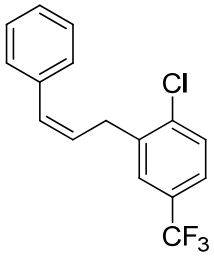


(E)-**3ad**

(E)-1-phenyl-3-(2-chloro-5-trifluoromethylphenyl)propene

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.51-7.49 (m, 1H), 7.45-7.42 (m, 2H), 7.38-7.36 (m, 2H), 7.32-7.29 (t, J = 7.2 Hz, 2H), 7.26-7.23 (m, 2H), 6.50 (d, J = 16.0 Hz, 1H), 6.32 (dt, J_1 = 15.6 Hz, J_2 = 6.8 Hz, 1H), 3.71 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.1, 138.0, 137.1, 132.7, 130.1, 129.5 (q, J_{CF} = 36.8 Hz), 128.7, 127.6, 127.4 (q, J_{CF} = 3.8 Hz), 126.4, 126.0, 124.7 (q, J_{CF} = 3.8 Hz), 123.9 (q, J_{CF} = 271.6 Hz), 37.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.4.

HRMS (EI) calc. for $C_{16}H_{12}F_3Cl$ $(M)^+$: 296. 0580, found: 296. 0582.

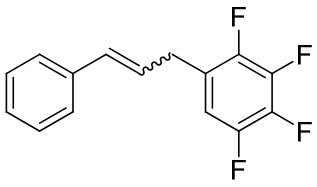


(Z)-**3ad**

(Z)-1-phenyl-3-(2-chloro-5-trifluoromethylphenyl)propene

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51-7.37 (m, 5H), 7.30-7.26 (m, 3H), 6.71 (d, J = 11.4 Hz, 1H), 5.80 (dt, J_1 = 11.7 Hz, J_2 = 7.2 Hz, 1H), 3.80 (d, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.6, 138.0 (q, J_{CF} = 1.5 Hz), 136.9, 132.0, 130.0, 129.5 (q, J_{CF} = 32.9 Hz), 128.8, 128.5, 127.7, 127.3, 126.8 (q, J_{CF} = 3.8 Hz), 124.5 (q, J_{CF} = 3.7 Hz), 123.9 (q, J_{CF} = 272.3 Hz), 32.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ -62.8.

HRMS (EI) calc. for $C_{16}H_{12}F_3Cl$ $(M)^+$: 296. 0580, found: 296. 0585.



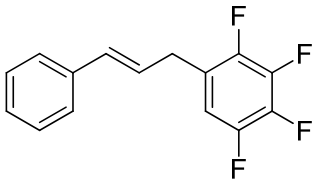
3ae

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.22 (m, 5H), 6.86-6.70 (m, 1H), 6.78 (d, J = 11.2 Hz, 0.56H), 6.47 (d, J = 14.6 Hz, 0.46H), 6.22 (dt, J_1 = 15.6 Hz, J_2 = 7.2 Hz, 0.45H), 5.70 (dt, J_1 = 11.6 Hz, J_2 = 7.2 Hz, 0.53H), 3.63 (d, J = 7.2 Hz, 1.11H), 3.53 (d, J = 7.2 Hz, 0.90H).

HRMS (EI) calc. for $C_{15}H_{10}F_4$ $(M)^+$: 266.0719, found: 266.0723.

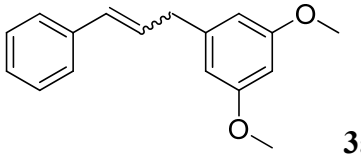
GC-MS: m/z: 228 $(M)^+$; E-isomer: 44.15% (area), Z-isomer: 55.85% (area)

^{1}H NMR spectral data of the (E)-product matched the spectral data of the known compound reported in the literatures.[14]



(E)-**3ae**

(E)-1-cinnamyl-2,3,4,5-tetrafluorobenzene (CAS: 1433415-33-8)[14]



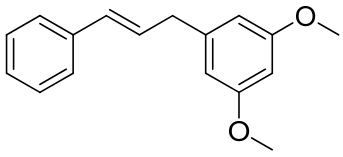
3af

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.20 (m, 5H), 6.60 (d, J = 15.6 Hz, 0.5H), 6.49-6.33 (m, 4H), 5.84 (dt, J_1 = 15.2 Hz, J_2 = 10 Hz, 0.35H), 3.77 (s, 6H), 3.62 (d, J = 10.8 Hz, 0.83H), 3.48 (d, J = 9.2 Hz, 1.09H).

HRMS (EI) calc. for $C_{17}H_{18}O_2$ $(M)^+$: 254.1307, found: 254.1311.

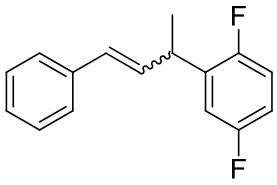
GC-MS: m/z: 254 $(M)^+$; E-isomer: 56.65% (area), Z-isomer: 43.35% (area).

^{1}H NMR spectral data of the (E)-isomer matched the spectral data of the known compound reported in the literatures.[15]



(E)-**3af**

(E)-1-cinnamyl-3,5-dimethoxybenzene (CAS: 1442416-32-1)[15]



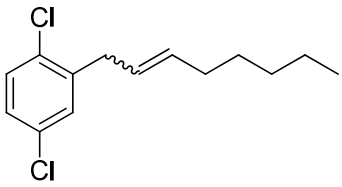
3lb

1-Phenyl-3-(2,5-difluorophenyl) butene

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.20 (m, 5H), 7.03-6.95 (m, 2H), 6.90-6.84 (m, 1H), 6.52 (d, *J* = 11.6 Hz, 0.55H), 6.45 (d, *J* = 16.0 Hz, 0.45H), 6.37-6.31 (m, 0.45H), 5.82 (t, *J* = 10.4 Hz, 0.55H), 4.29-4.20 (m, 0.55H), 3.99-3.92 (m, 0.45H), 1.45 (d, *J* = 6.8 Hz, 1.5H), 1.36 (d, *J* = 6.8 Hz, 1.5H).

HRMS (EI) calc. for $C_{16}H_{14}F_2$ $(M)^+$: 244.1064, found: 244.1068.

GC-MS: m/z: 244 $(M)^+$; E-isomer: 49.39% (area), Z-isomer: 50.61% (area).

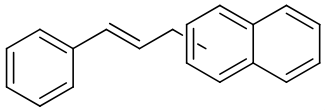


3kc

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.09 (m, 3H), 5.62-5.46 (m, 2H), 3.45 (d, *J* = 9.6 Hz, 1.24H), 3.39 (d, *J* = 6.0 Hz, 0.75H), 2.16-2.00 (m, 2H), 1.42-1.26 (m, 6H), 0.94-0.87 (m, 3H).

HRMS (EI) calc. for $C_{14}H_{18}Cl_2$ $(M)^+$: 256.0786, found: 256.0784.

GC-MS: m/z: 256 $(M)^+$; E-isomer: 55.46% (area), Z-isomer: 44.54% (area).

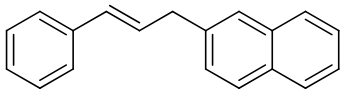


3ah+**3ah′**

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.77 (m, 8H), 7.47-7.20 (m, 21H), 6.65 (d, J = 15.2 Hz, 1H), 6.53-6.37 (m, 2.7H), 5.94 (dt, J_1 = 15.2 Hz, J_2 = 10.0 Hz, 1H), 4.10 (d, J = 8.8 Hz, 0.29H), 3.98 (d, J = 6.0 Hz, 1H), 3.83 (d, J = 10.0 Hz, 2H), 3.70 (d, J = 8.0 Hz, 2.6H).

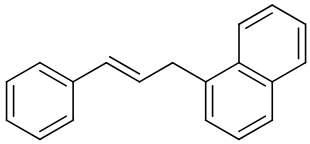
GC-MS: m/z: 244 $(M)^+$; **3ah** E-isomer: 44.25% (area), Z-isomer: 32.41% (area), **3ah′** E-isomer: 14.54% (area), Z-isomer: 8.80% (area).

^{1}H NMR spectral data of the isolated products matched the spectral data of known compounds reported in the literatures.[16]



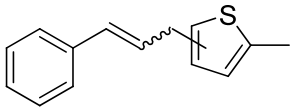
(E)-**3ah**

(E)-1-phenyl-3-(2-naphenyl)propene (CAS: 5751-33-7)[16]



(E)-**3ah′**

(E)-1-phenyl-3-(1-naphenyl)propene (CAS: 5751-29-1)[16]

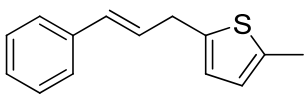


3ai

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.23 (m, 6H), 6.86 (d, J = 3.6 Hz, 1H), 6.63-6.57 (m, 4H), 6.33 (dt, J_1 = 20.8 Hz, J_2 = 8.8 Hz, 0.5H), 3.66-3.62 (m, 1H), 3.74 (d, J = 10.0 Hz, 1.2H), 3.64 (d, J = 8.8 Hz, 1H), 3.55 (d, J = 10.4 Hz, 0.14H), 3.45 (d, J = 9.2 Hz, 0.16H), 2.44 (s, 7.8H).

GC-MS: m/z: 214 $(M)^+$; **3ai** E-isomer: 41.47% (area), Z-isomer: 41.40% (area); **3ai′** E-isomer: 9.17% (area), Z-isomer: 7.96% (area).

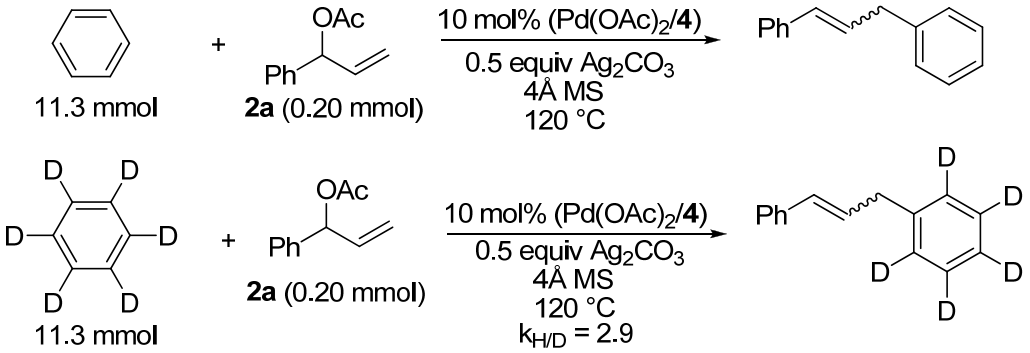
^{1}H NMR spectral data of the isolated products matched the spectral data of known compounds reported in the literatures.[17]



E-**3ai**

(E)-3-(5-methylthiophen-2-yl)-1-phenylpropene (CAS: 807370-02-1)[17]

KIE reaction



$Pd(OAc)_2$ (4.5 mg, 0.020 mmol), $Cu(OAc)_2$ (36.2 mg, 0.20 mmol), ligand **4** (3.9 mg, 0.020 mmol), **2a** (35.2 mg, 0.20 mmol), 4Å molecular sieve (20 mg), benzene (11.3 mmol) or benzene-d_6 (11.3 mmol) was added to a solution tube and the mixture was heated to 120 °C and stirred for 10 to 90 min. After immediately cooling to room temperature, the yield of product was determined with 1,3,5-trimethylbenzene as the internal standard by GC. The obtained yields were plotted as concentration [allylic arene] vs. time t (Figures 1 and 2). From these diagrams, the following initial rates were calculated:

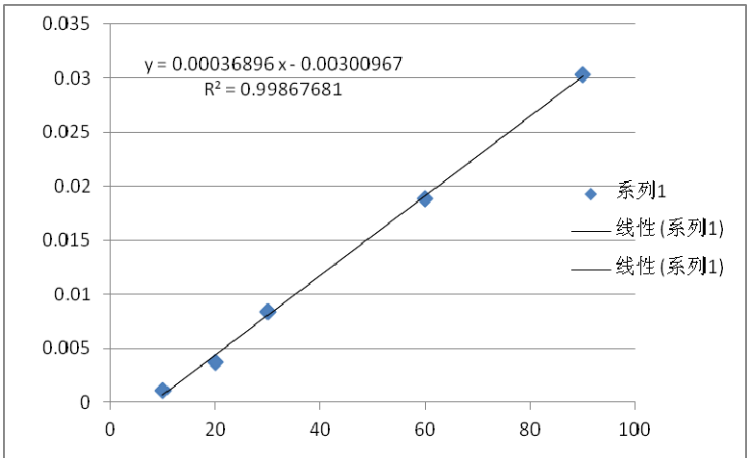


Fig. 1: The reaction of benzene with **2a**.

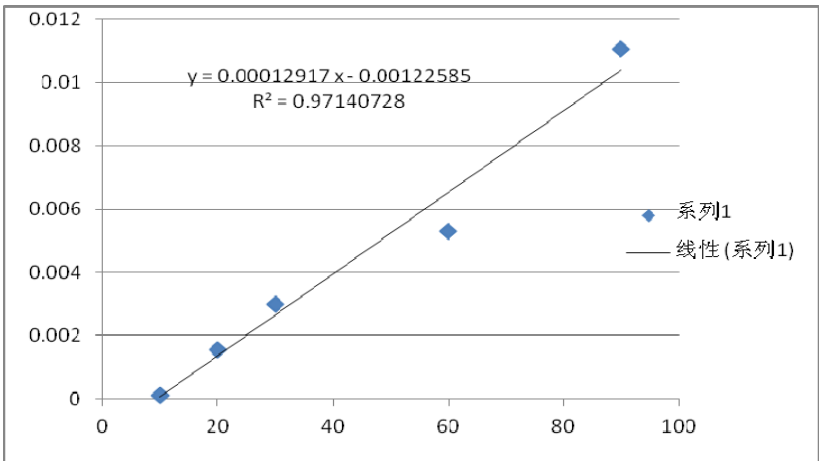
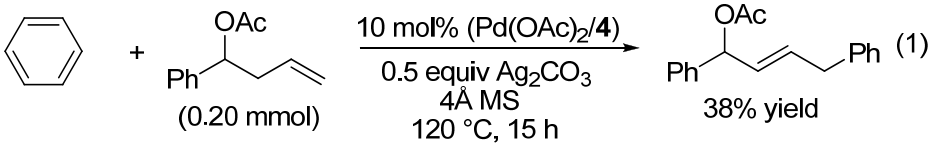


Fig. 2: The reaction of deuterated-benzene with **2a**.

$K_H = 3.69\times 10^{-4}$ mmol·mL^{-1}·min^{-1}; $K_D = 1.29 \times 10^{-4}$ mmol·mL^{-1}·min^{-1}

$K_H/K_D = 2.9$

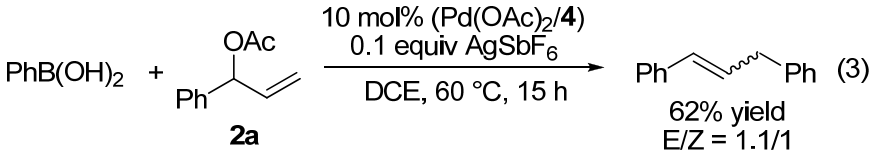
Eq. 4. Reaction of a homoallylic acetate with benzene under the optimum conditions.



The reaction was carried out under the optimum conditions.

CAS: 849590-71-2. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.21 (m, 10H), 6.43 (d, J = 15.6 Hz, 1H), 6.08 (dt, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1H), 5.88 (t, J = 7.2 Hz, 1H), 2.83-2.68 (m, 2H), 2.09 (s, 3H).

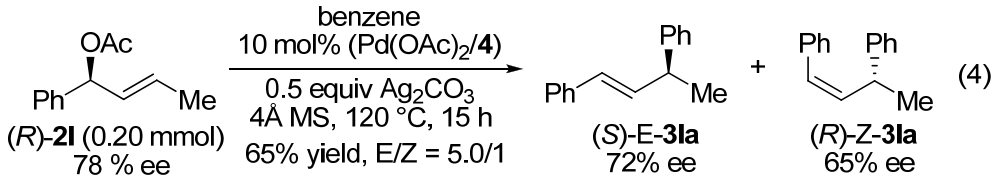
Eq. 3. Reaction of phenylboronic acid with allylic acetate 2a catalyzed by Pd/4.



$Pd(OAc)_2$ (4.5 mg, 0.02 mmol), $AgSbF_6$ (6.8 mg, 0.02 mmol), ligand **4** (3.9 mg, 0.02 mmol) and DCE (2 mL) were added to a solution tube and the resulting solution was stirring for 1 min, then **2a** (35.2 mg, 0.20 mmol) and phenylboronic acid (24.2 mg, 0.20 mmol) was added and the resulting solution was heated to 60 °C and reacted for 15 hours. After cooling to room temperature, the mixture was filtrated through a

pad of silica gel and washed with ethyl acetate. The filtrate was concentrated under vacuum, and the residue was purified by silica gel flash column chromatography to afford the E/Z-isomers as a mixture (24.1 mg, 62% yield).

Eq. 4. Reaction of enantioenriched allylic acetate with benzene under the optimum conditions.



(*S*)-E-**3la** and (*R*)-Z-**3la** were obtained in 72% ee and 65% ee. The enantiomeric excess of products were determined by chiral HPLC analysis (OD column, hexane: *i*-PrOH = 99.9:0.1, t_r[(*R*)-Z-isomer] = 12.74 min, t_r[(*S*)-Z-isomer] = 15.92 min, t_r[(*S*)-E-isomer] = 17.77 min, t_r[(*R*)-E-isomer] = 19.58 min). The absolute of configuration of isomers were determined by comparison of their HPLC retention time with that reported in literature.[16,18]

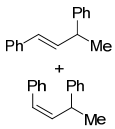
==== Shimadzu LCsolution Analysis Report ====

D:\ych\ych-17-97-1-OD-1-9991-1.lcd

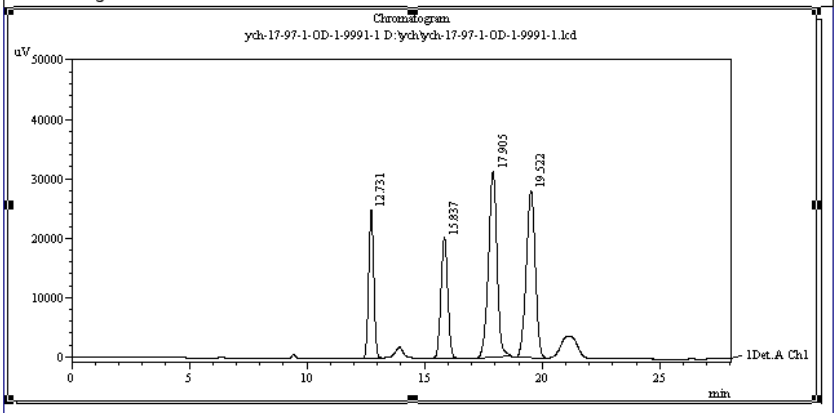
Sample Name : ych-17-97-1-OD-1-9991-1 Date:

Column: The mobile phase:

Velocity: The detection wavelength:



<Chromatogram>



Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.731	376722	24869	16.210
2	15.837	406933	20290	17.510
3	17.905	788960	31190	33.949
4	19.522	751333	28134	32.330
Total		2323948	104483	100.000

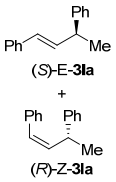
==== Shimadzu LCsolution Analysis Report ====

D:\ych\ych-18-40-4A-OD-1-9991-1.lcd

Sample Name : ych-18-40-4A-OD-1-9991-1 Date:

Column: The mobile phase:

Velocity: The detection wavelength:



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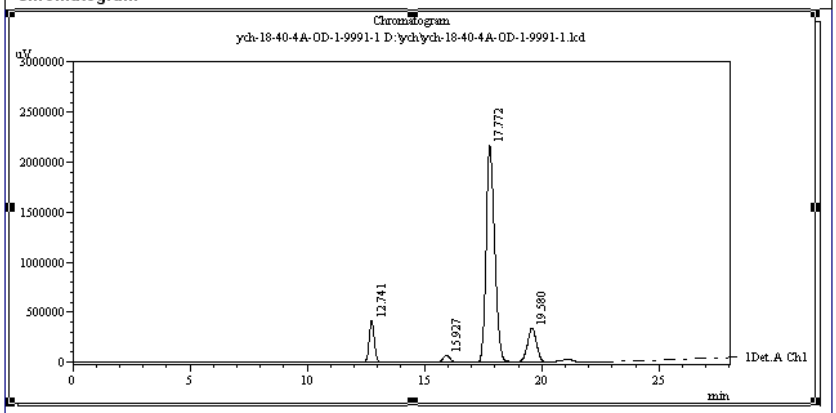


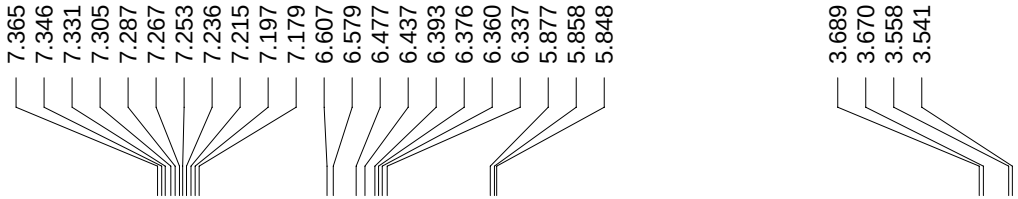
Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.741	6322897	414771	8.914
2	15.927	1347737	66761	1.900
3	17.772	54326895	2162642	76.593
4	19.580	8932010	337898	12.593
Total		70929539	2982072	100.000

Referenes

1. (a) Krapcho, P.; Sparapani, S. *J. Hetero. Chem.* **2008**, *45*, 1167. (b) Tomon, T. Koizumi, T.-A.; Tanaka, K. *Eur. J. Inorg. Chem*. **2005**, 285. (c) Vangapandu, S., Jain, M., Jain, R., Kaur, S.; Singh, P. P. *Bioorg. Med. Chem*. **2004**, *12*, 2501. (d) Zhang, Y.-H.; Shi, B.-F.; Yu, J.-Q. *J. Am. Chem. Soc*. **2009**, *131*, 5072.
2. Sekine, M.; Ilies, L.; Nakamura, E. *Org. Lett.* **2013**, *15*, 714.
3. Elizabeth, F.; Cornelius, O.; David, T.; Ashok, V. *Chem.–Eur. J.* **2012**, *18*, 8774.
4. Maddali, R.; Debasis, B.; Somnath, G. *J. Organomet. Chem.* **2010**, *695*, 1518.
5. Nobujiro, S.; Makoto, S.; Yuho, T. *Chem. Lett.* **1990**, *12*, 2207.
6. Yang, H.; Sun, P.; Zhu, Y.; Yan, H.; Lu, L.; Mao, J. *Chem. Commun.* **2012**, *48*, 7847.
7. Tiago, R.; Francisca, L.; Rui, M. *Synth. Commun.* **2012**, *42*, 747.
8. Naoya, F.; Yamamoto, Y. *J. Org. Chem.* **1999**, 64, 4095.
9. Shen, Y.; Yao, J. *J. Org. Chem.* **1996**, *61*, 8659.
10. (a) Lpez, M.; Varela, M.; Sarandeses, L.; Sestelo J. *Chem. Eur. J.* **2010**, *16*, 9905-9909.
11. (a) Falck, J.; Muralidhar, B.; Sylesh K.; Dale, S. *J. Org. Chem.* **2001**, *66*, 7148. (b) Kobayashi, Y.; Mizojiri, R.; Ikeda, E. *J. Org. Chem.* **1996**, *61*, 5391.
12. Zhao, J.; Ye, J.; Zhang, Y. *Adv. Synth. Catal.* **2013**, *355*, 491.
13. Riveiros, R.; Tato, R.; Pérez Sestelo, J.; Sarandeses, L. A. *Eur. J. Org. Chem.* **2012**, 3018.
14. Yu, Y.; Fan, S.; Zhang, X. *Chem.–Eur. J.* **2012**, *18*, 14643.
15. Robbins, Daniel W.; Hartwig, J. F. *Angew. Chem. Int. Ed*. **2013**, *52*, 933.
16. Man, B.; Yong, W.; Tian, S. *Angew. Chem. Int. Ed.* **2012**, *51*, 2968.
17. Onodera, G. Imajima, H.; Yamanashi, M.; Nishibayashi, Y.; Hidai, M.; Uemura, S. *Organometallics* **2004**, *23*, 5841.
18. Lloyd-Jones, G. C.; Butts, C. P. *Tetrahedron*, **1998**, *54*, 901.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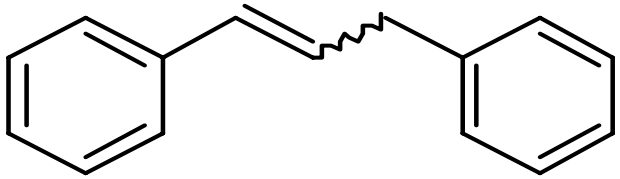
3.541



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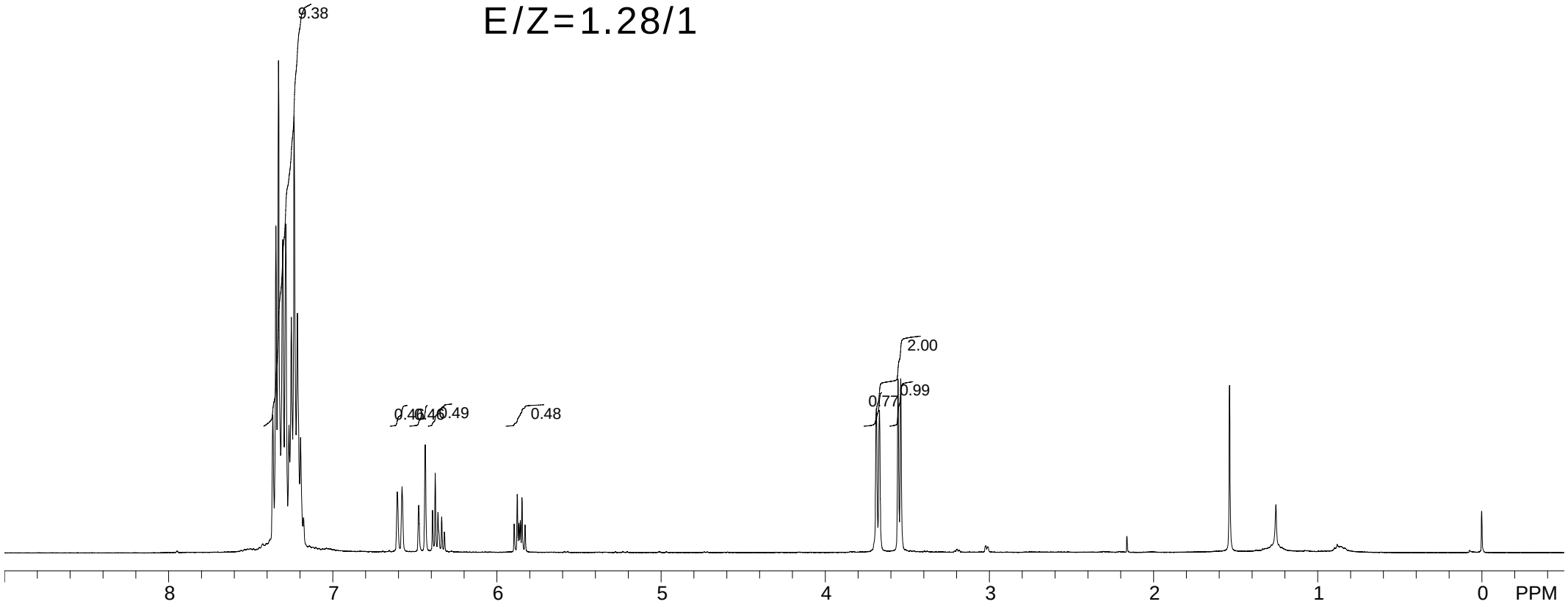
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2
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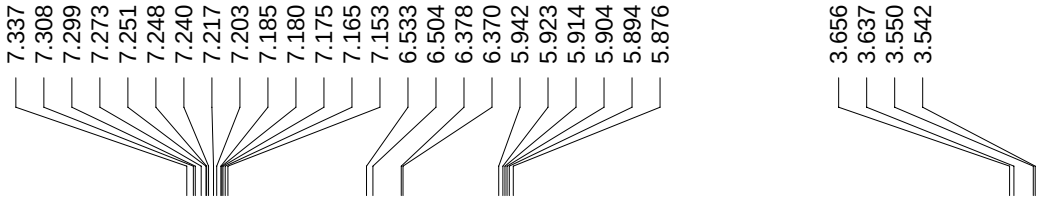
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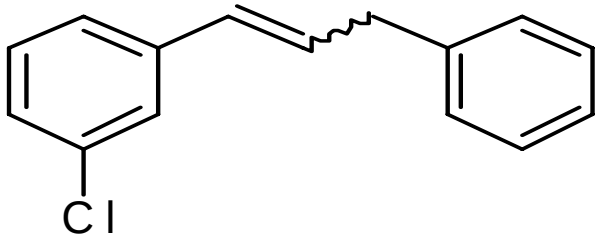
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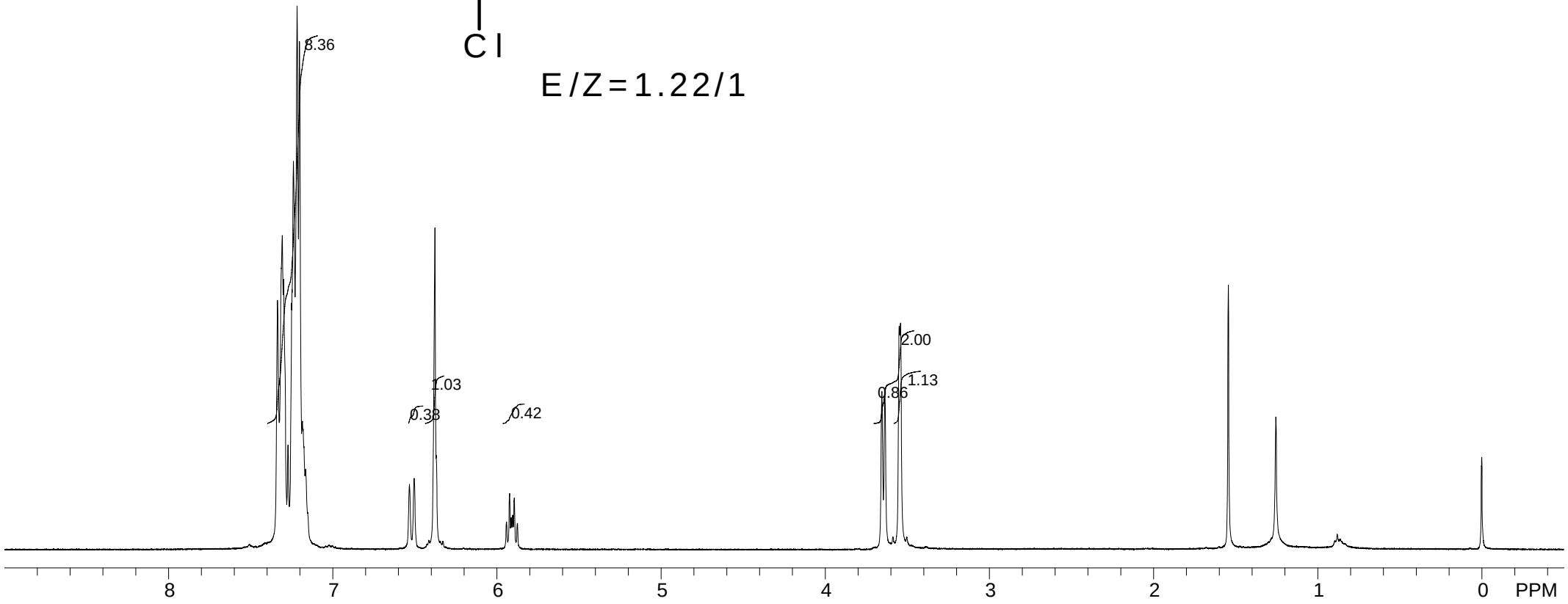
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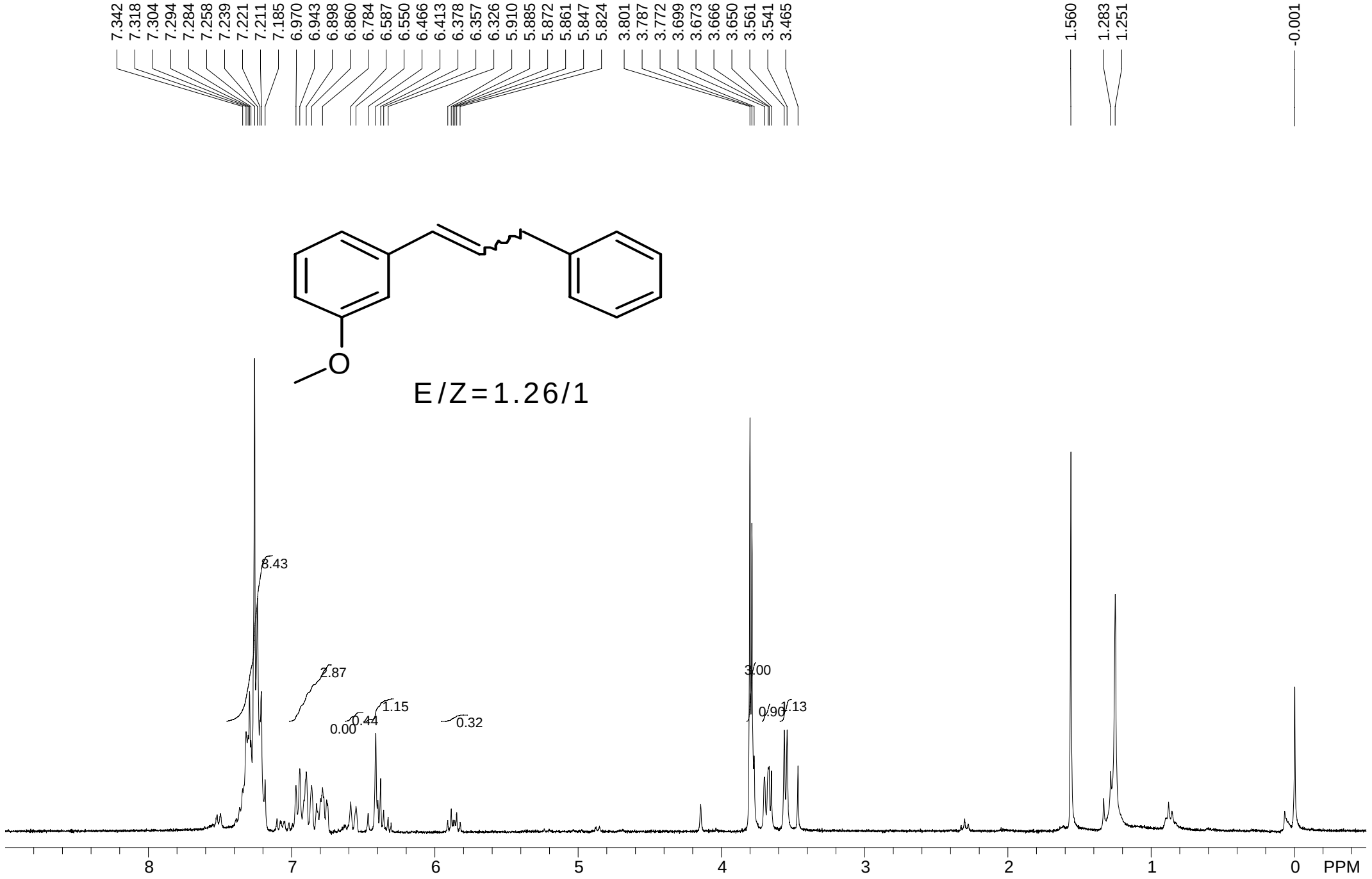
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6.550
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6.413
6.378
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6.326
5.910
5.885
5.872
5.861
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5.824
3.801
3.787
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3.650
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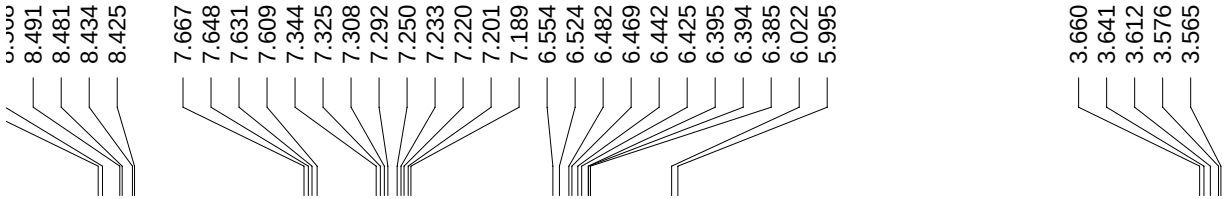
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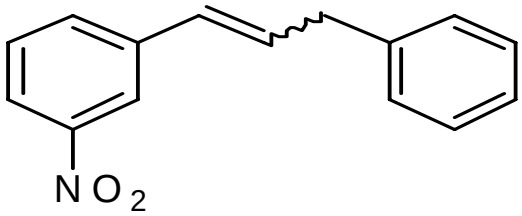
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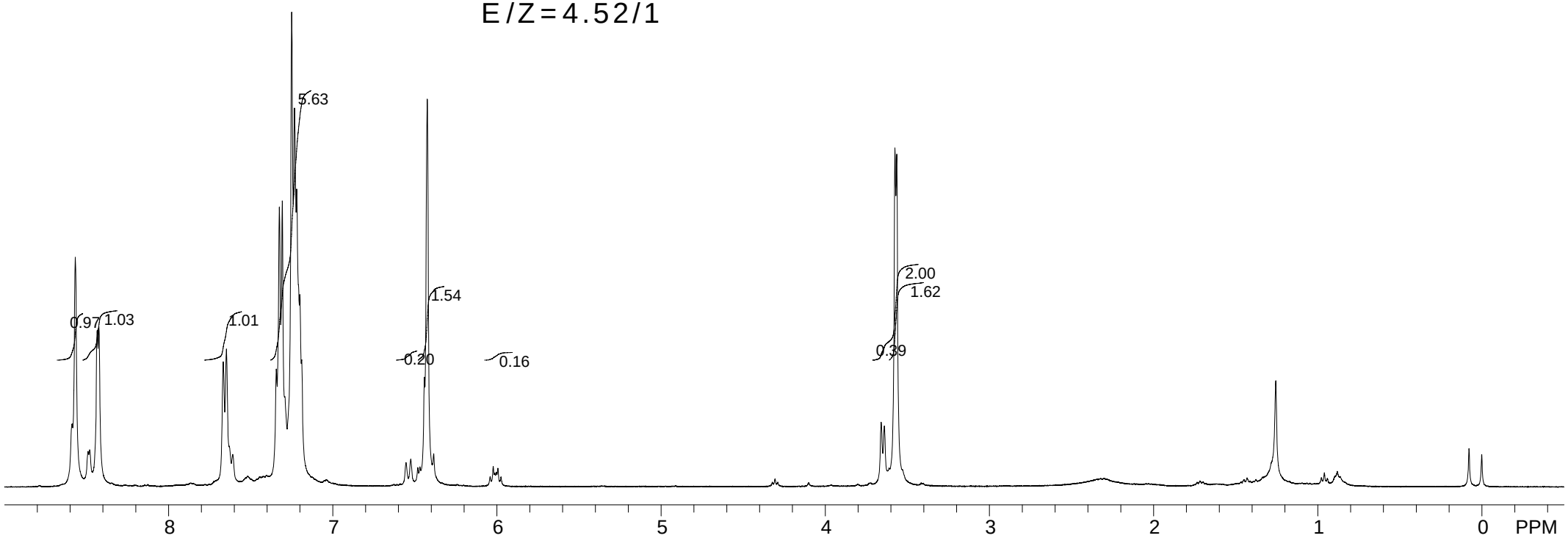
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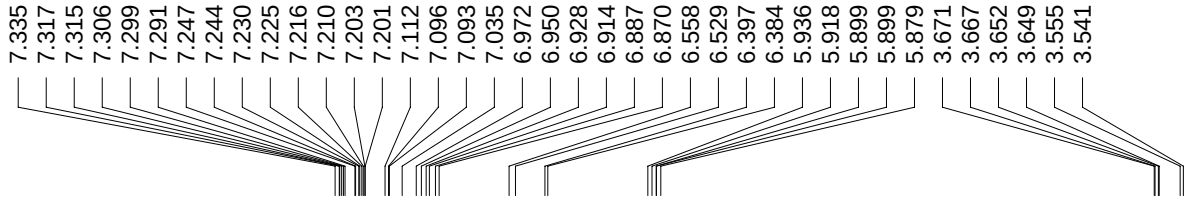
2
1
0
PPM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7.093
7.035
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6.950
6.928
6.914
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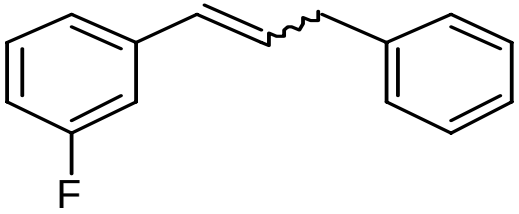
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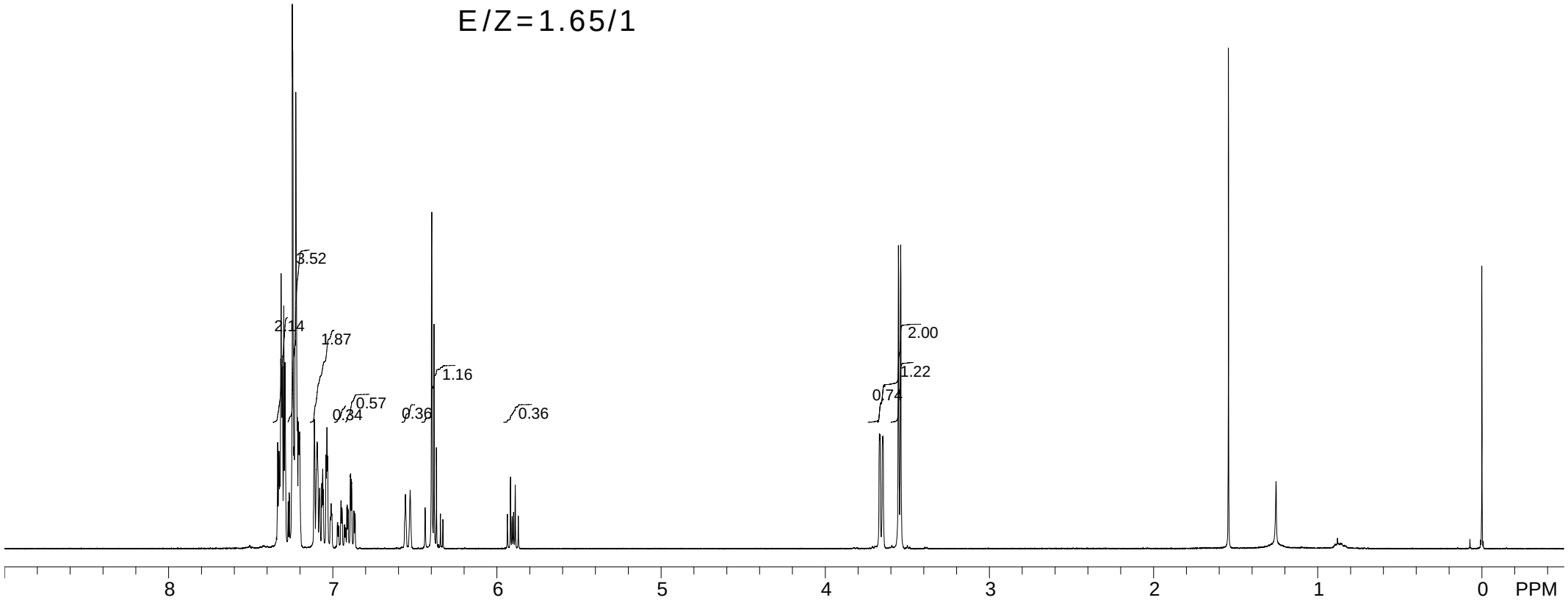
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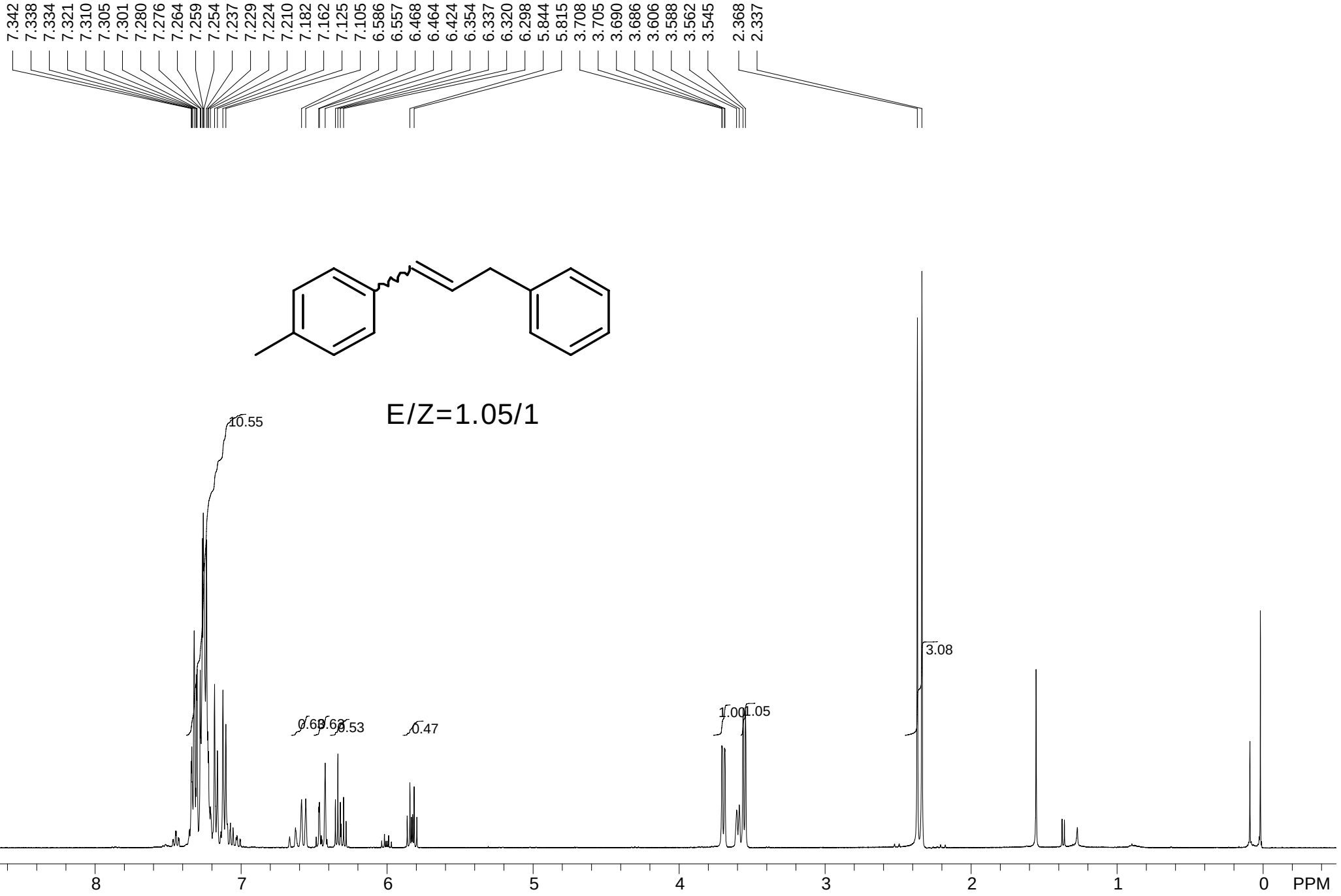
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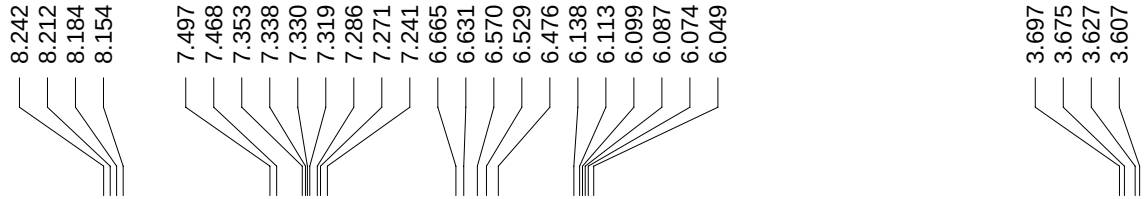
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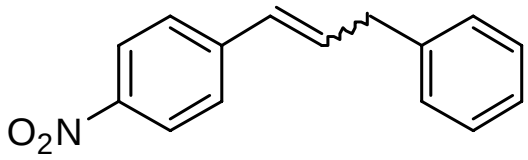
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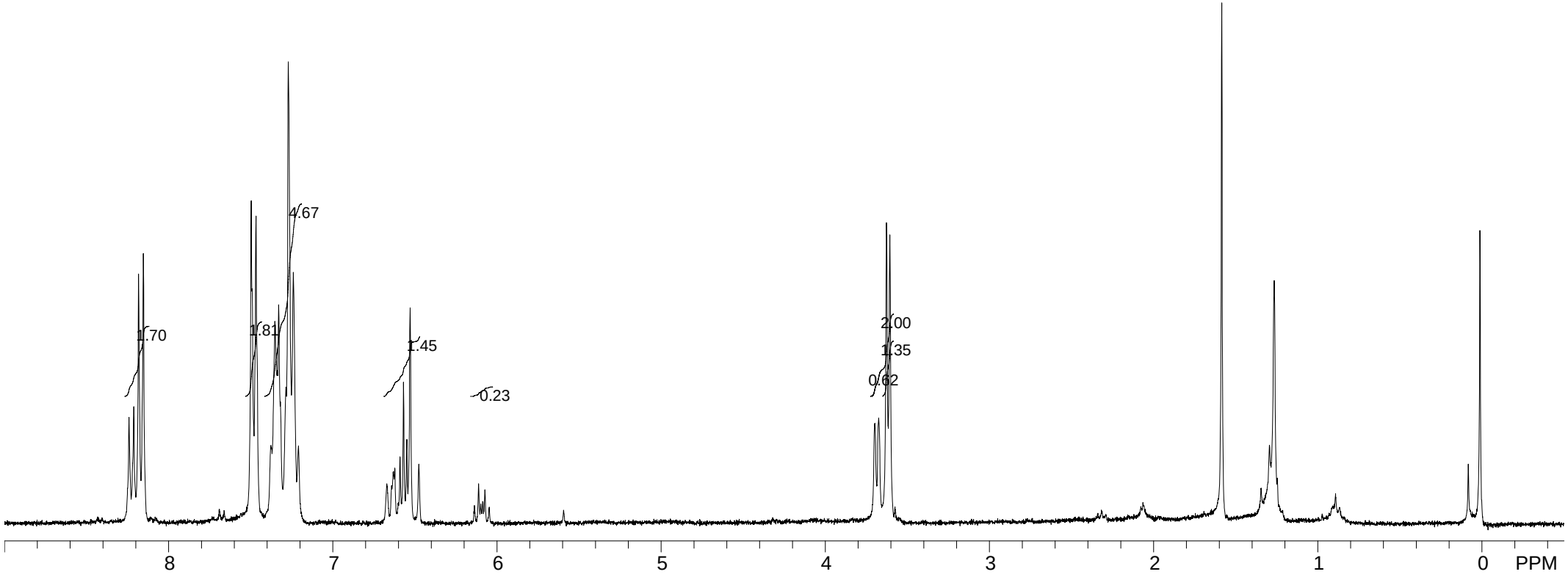
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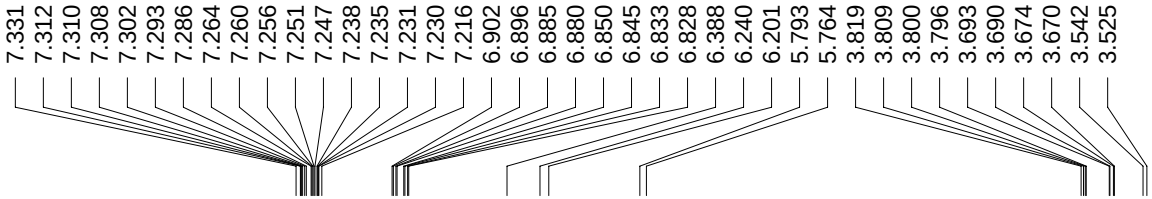
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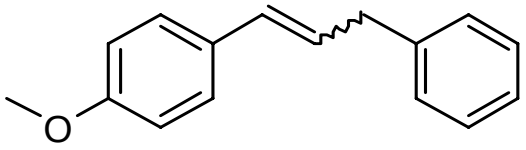
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E/Z=1.05/1

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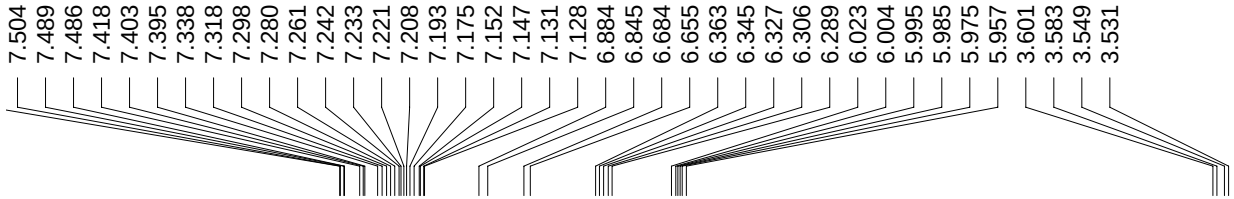
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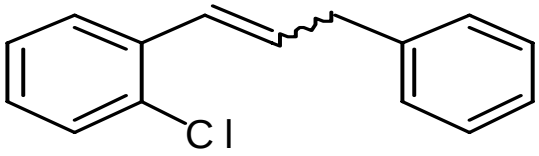
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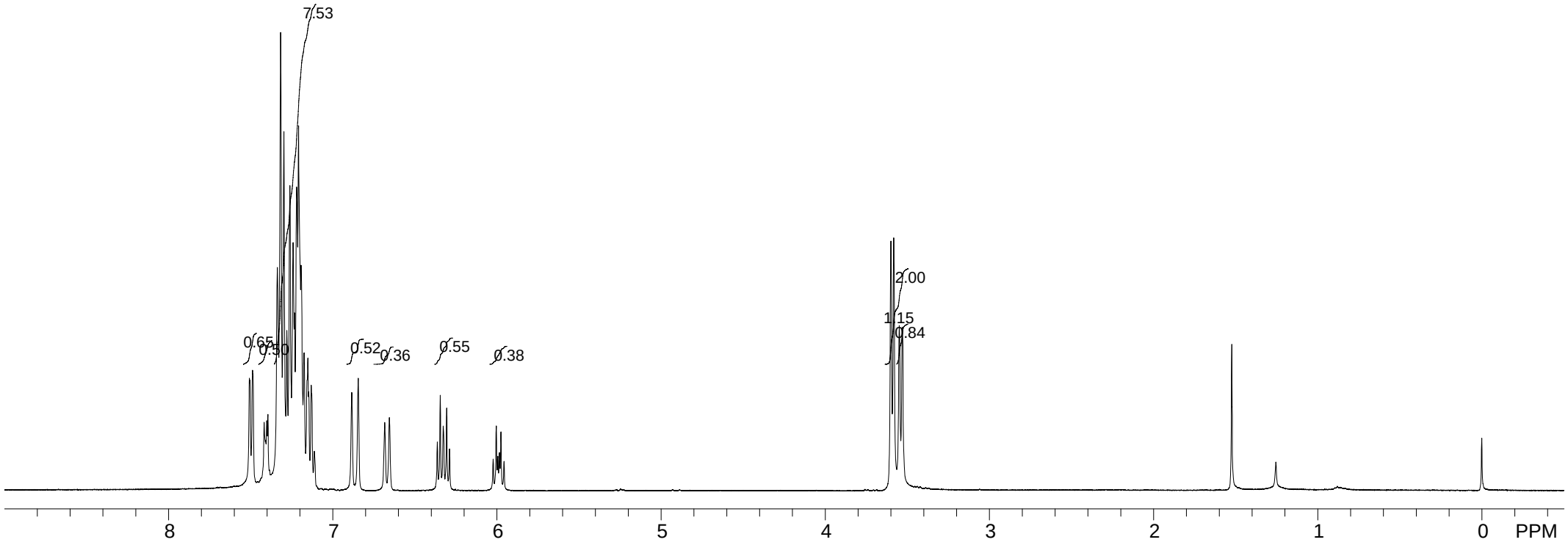
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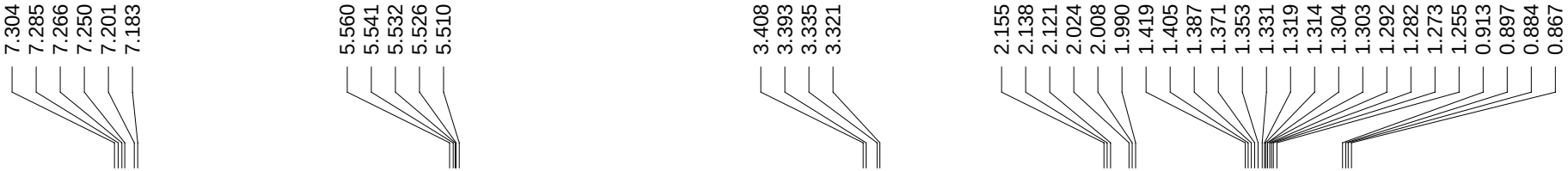
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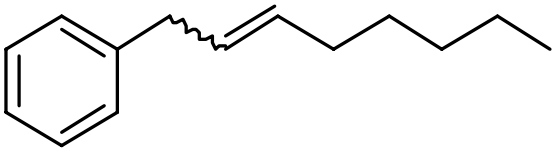

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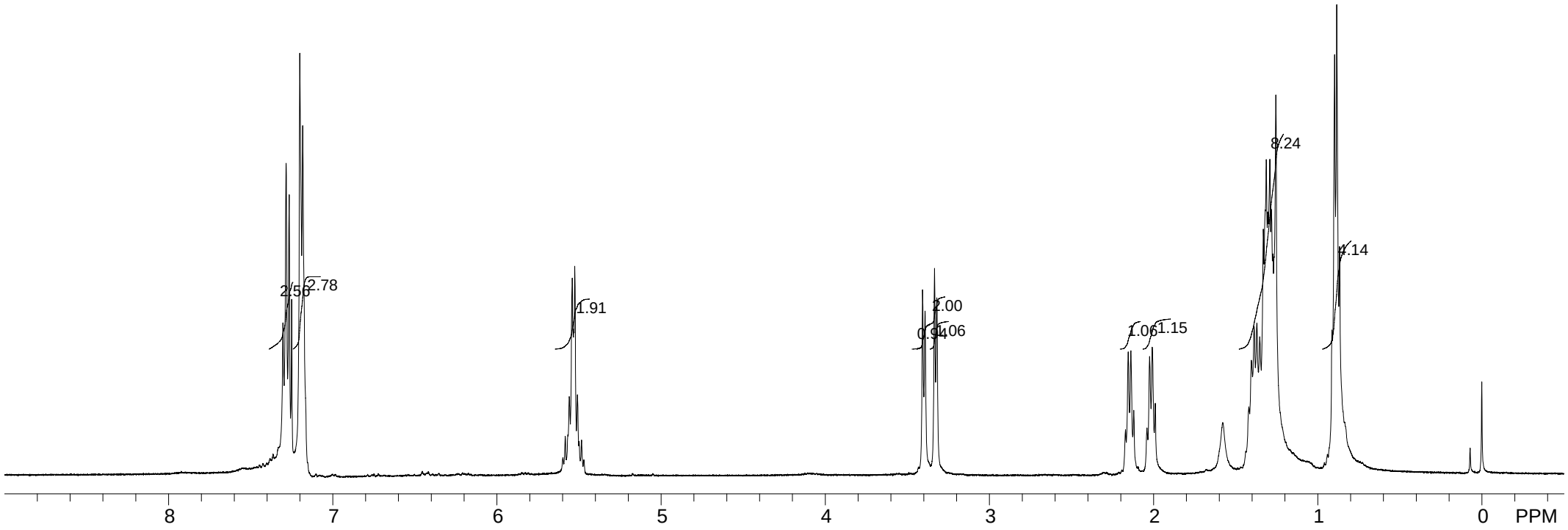
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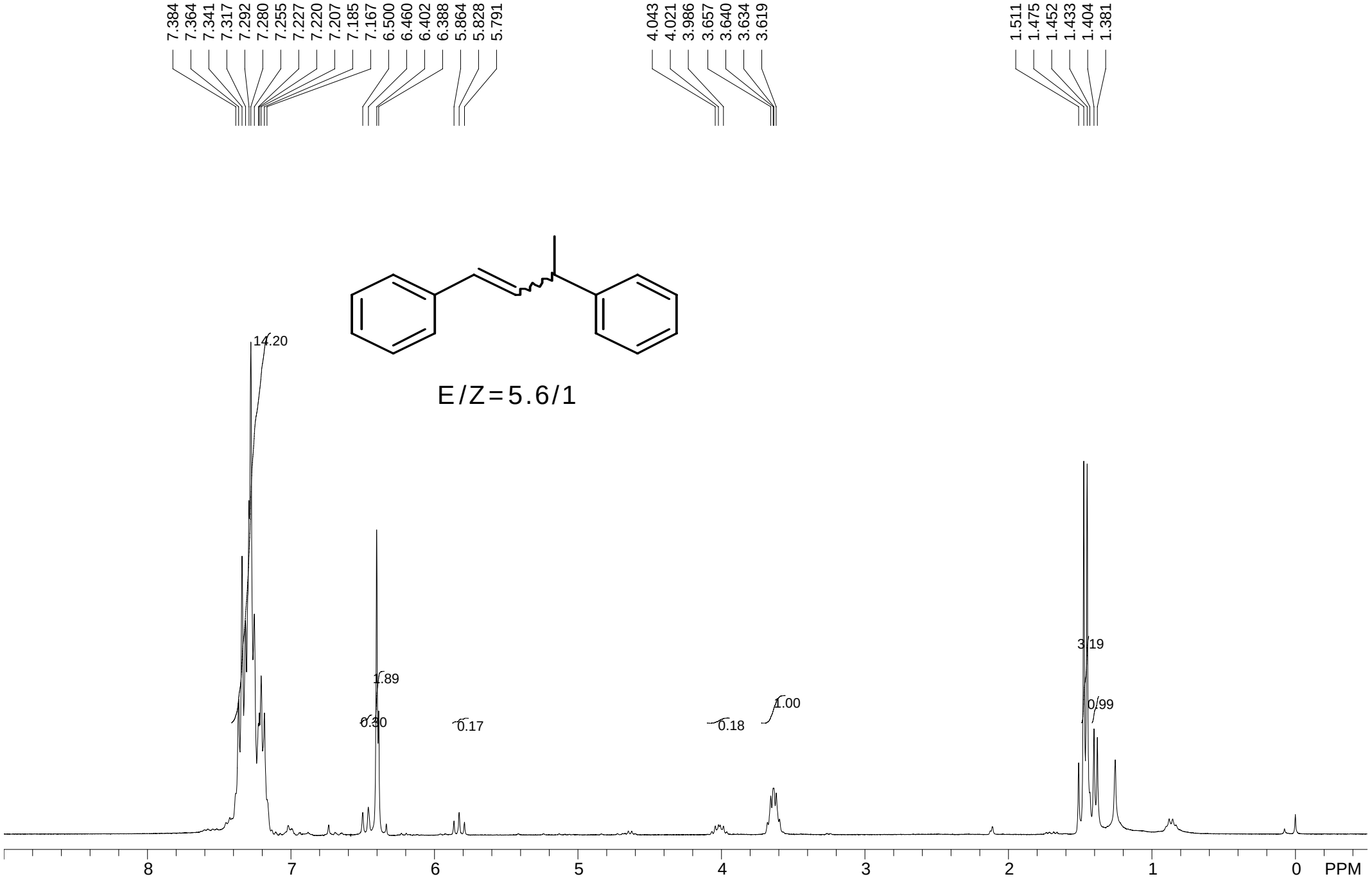
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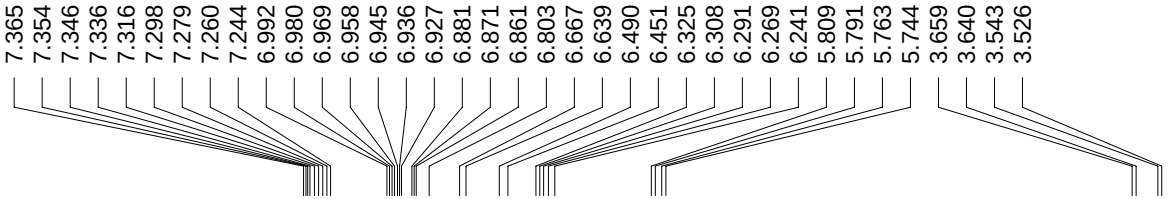
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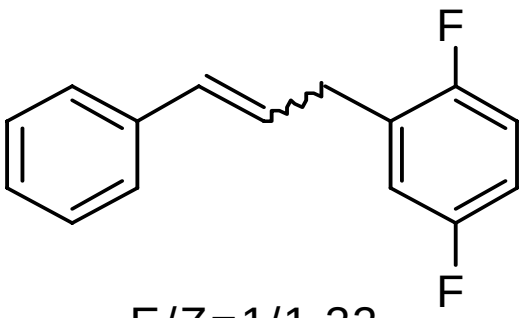
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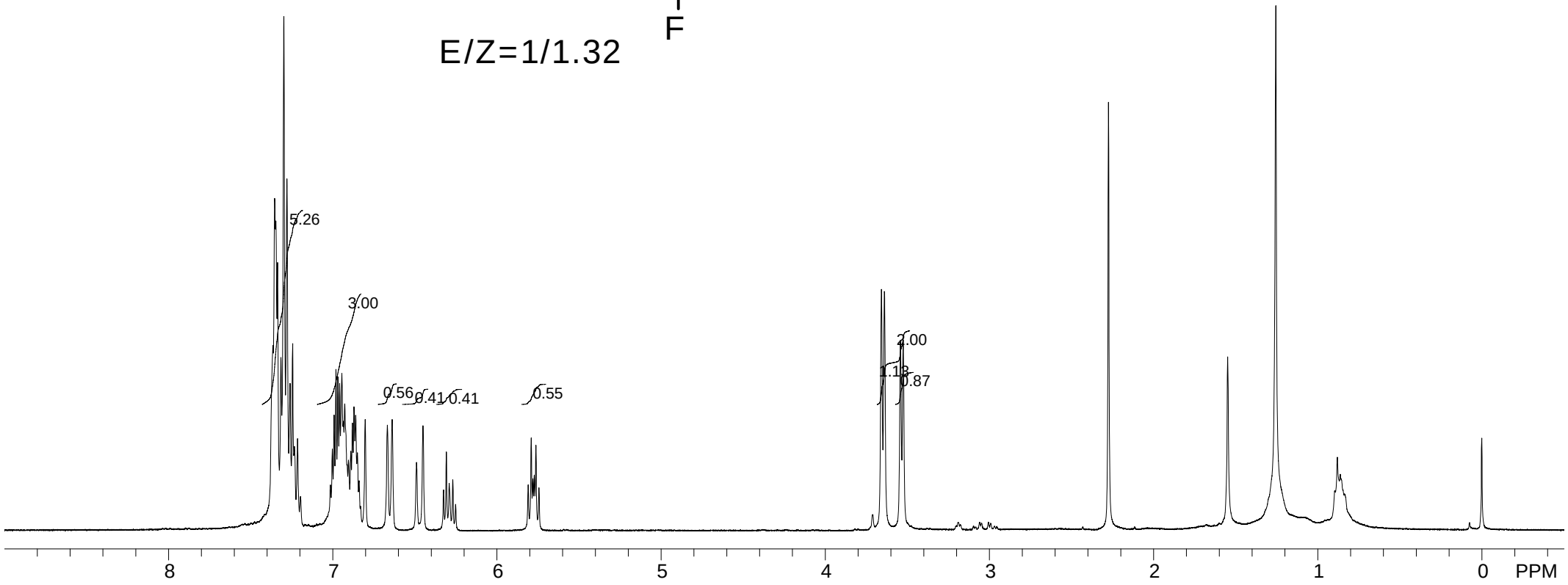
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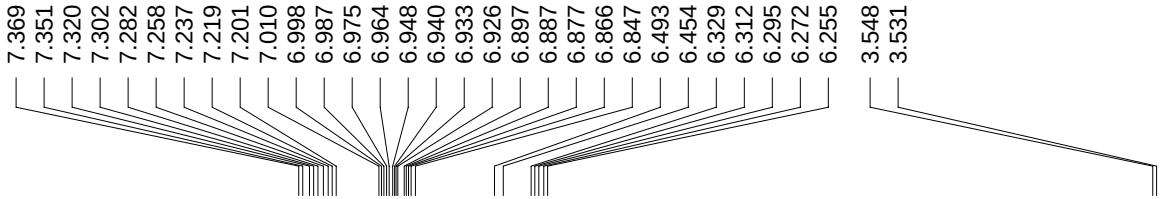
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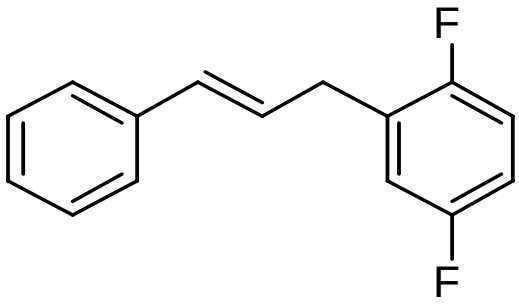
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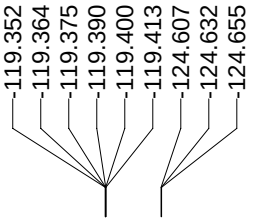
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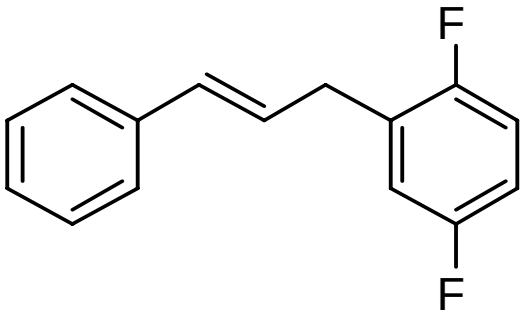
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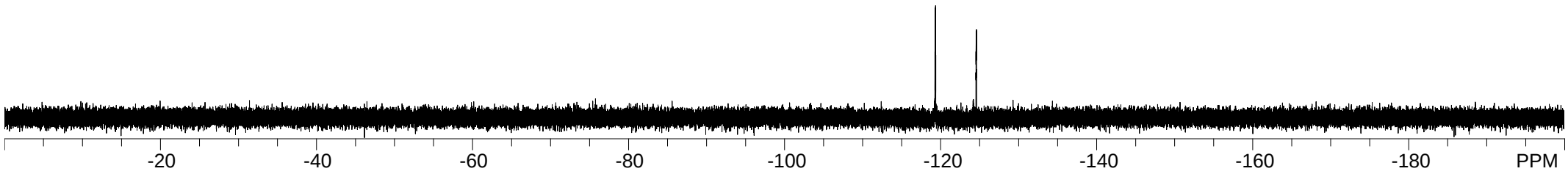
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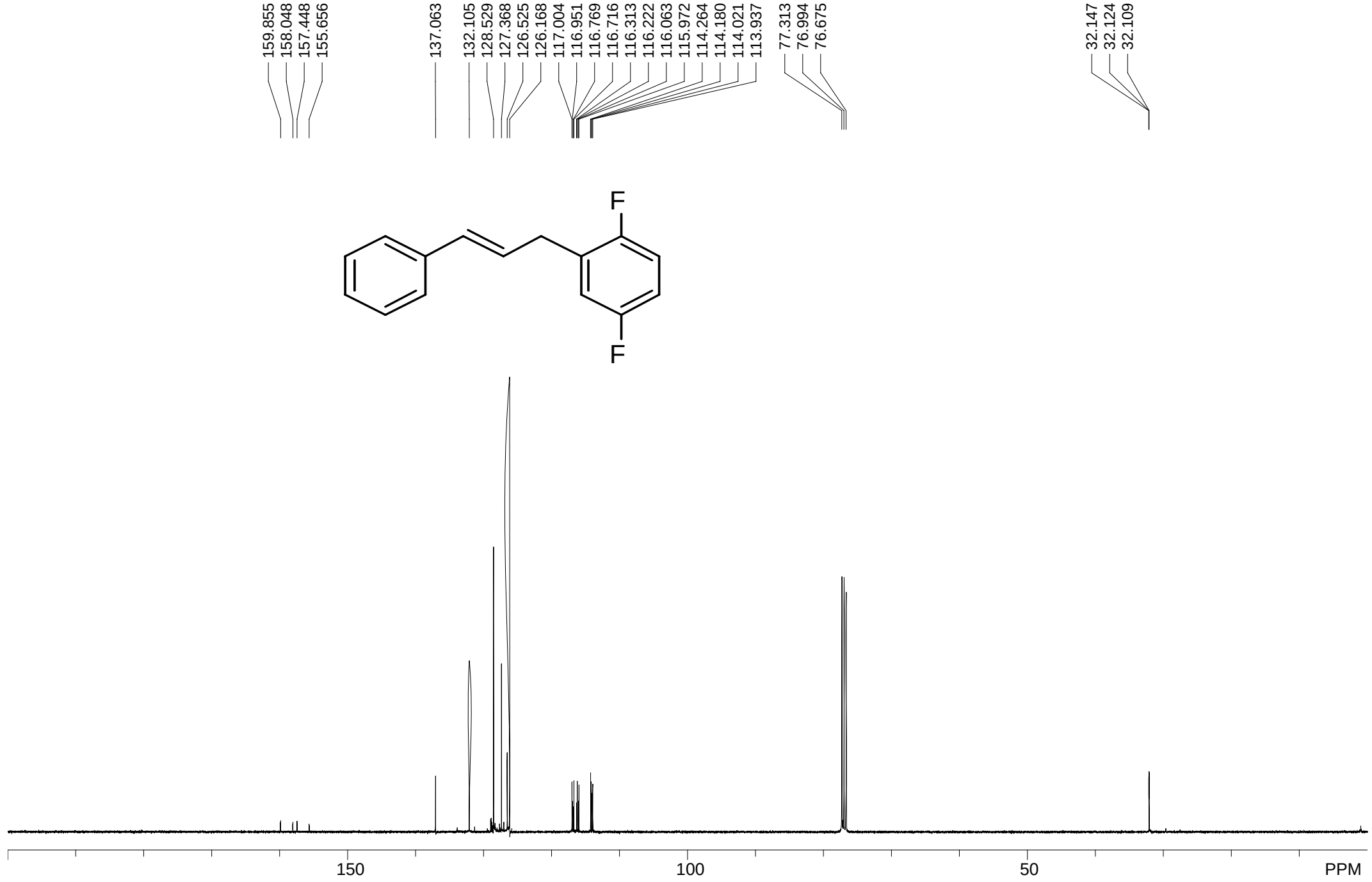
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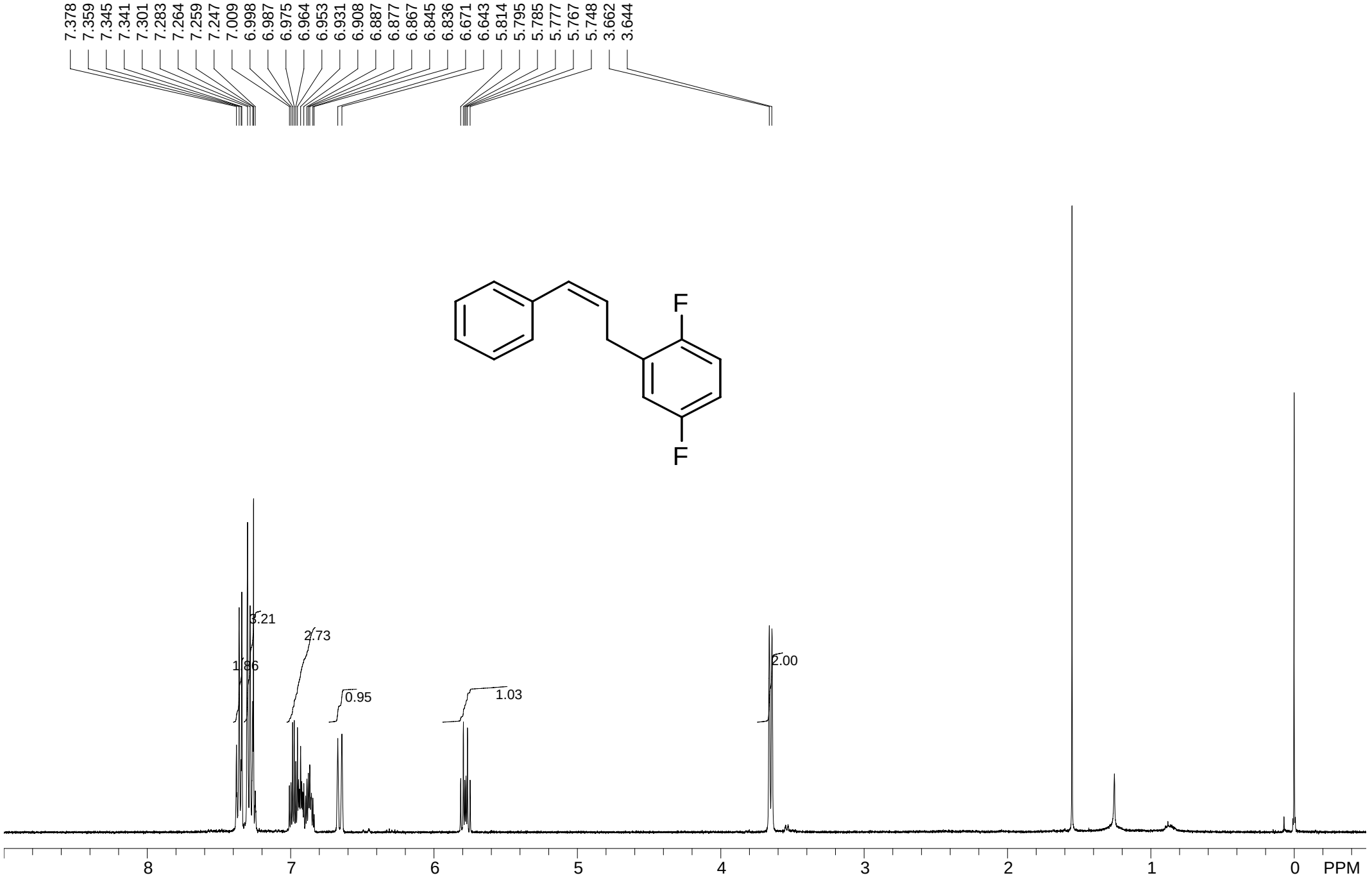
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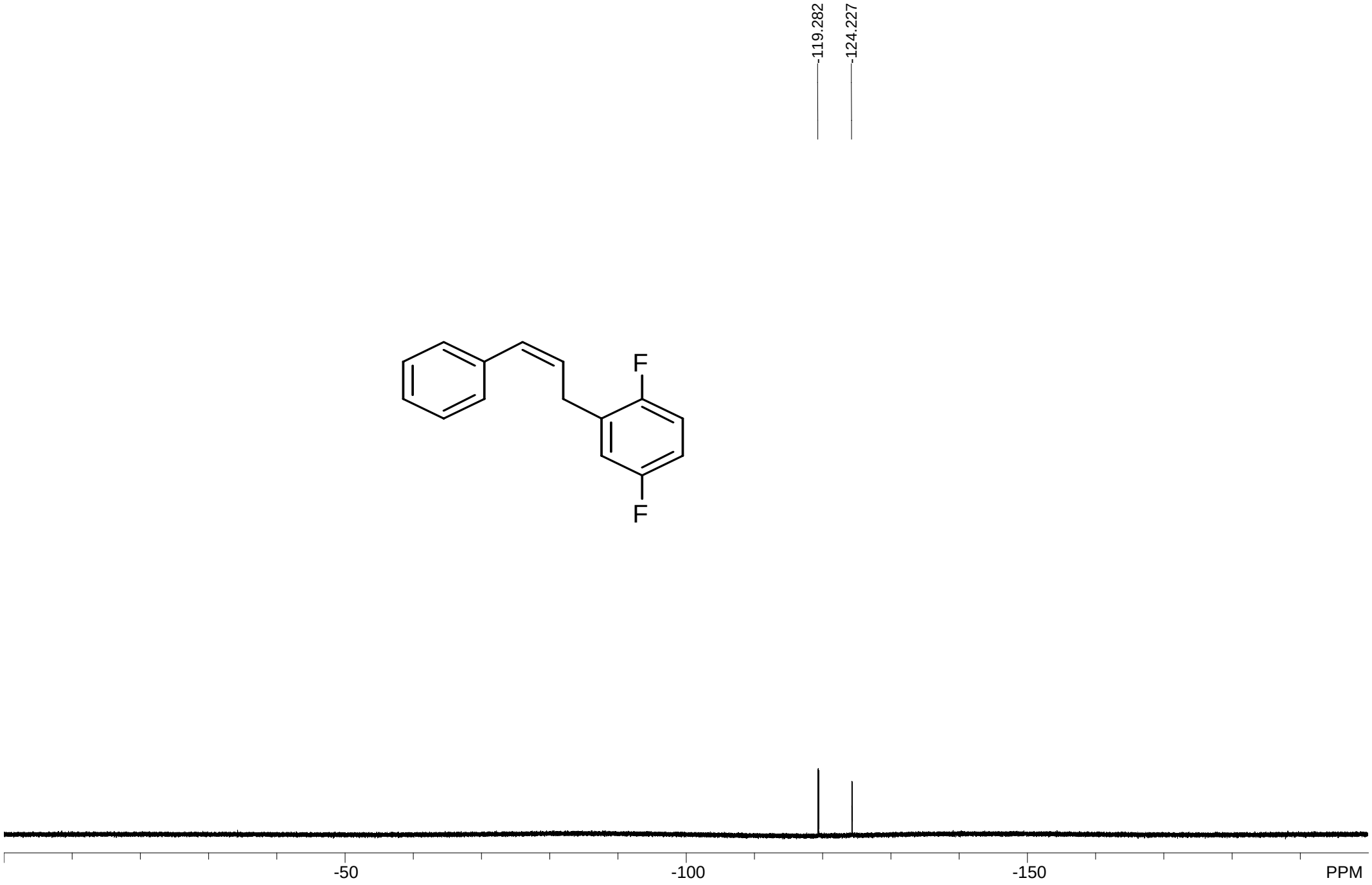
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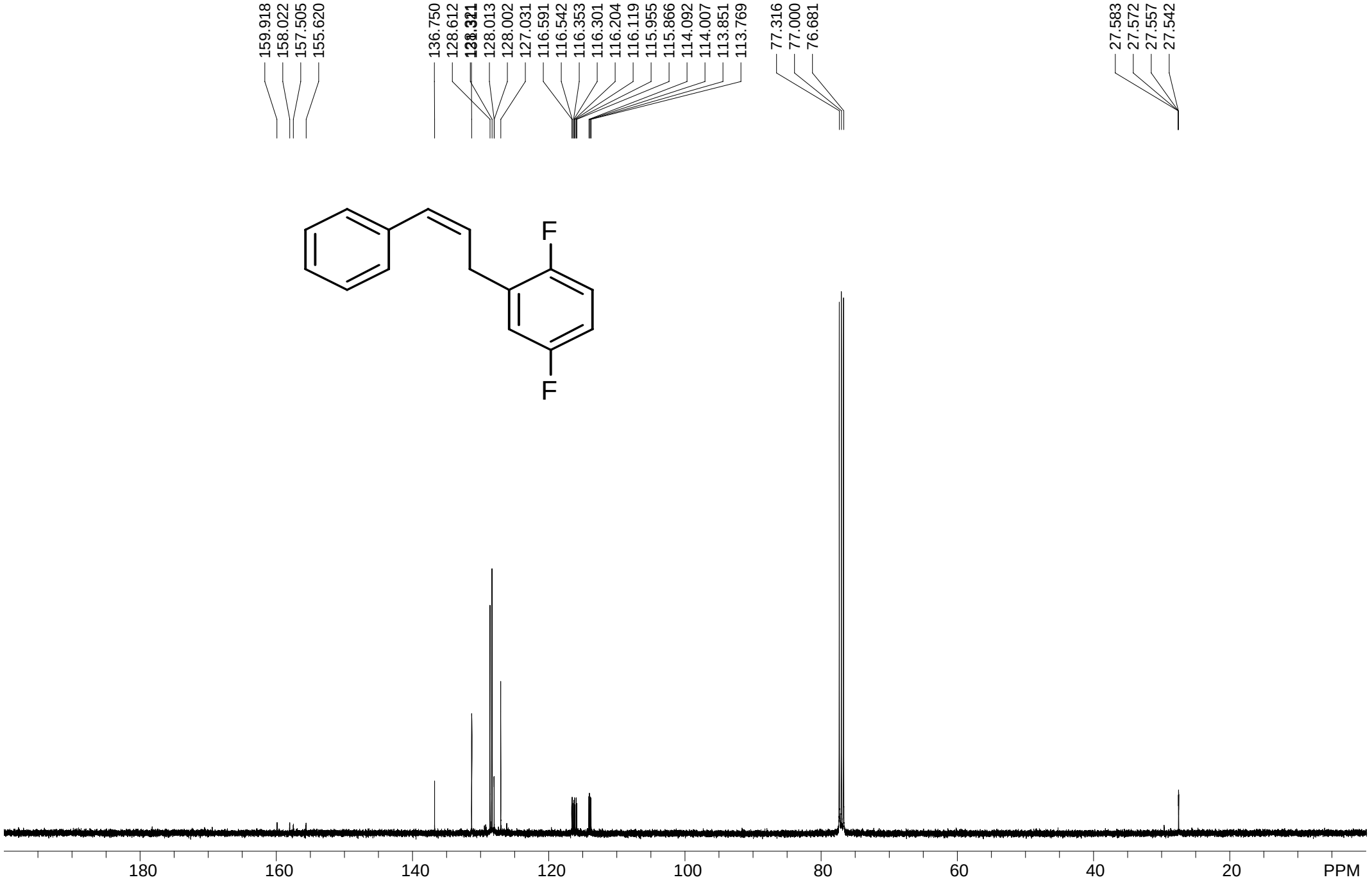
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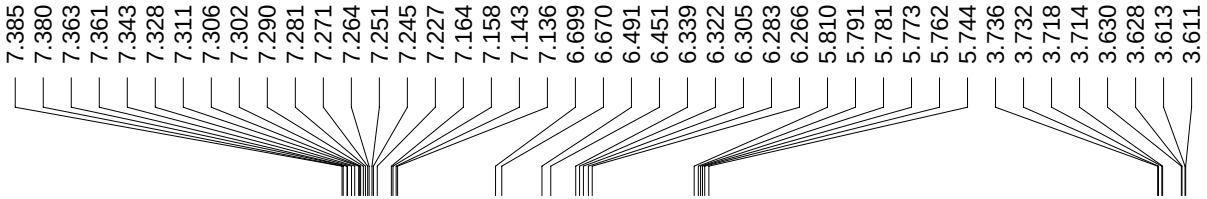
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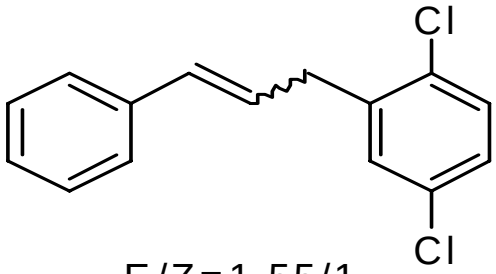
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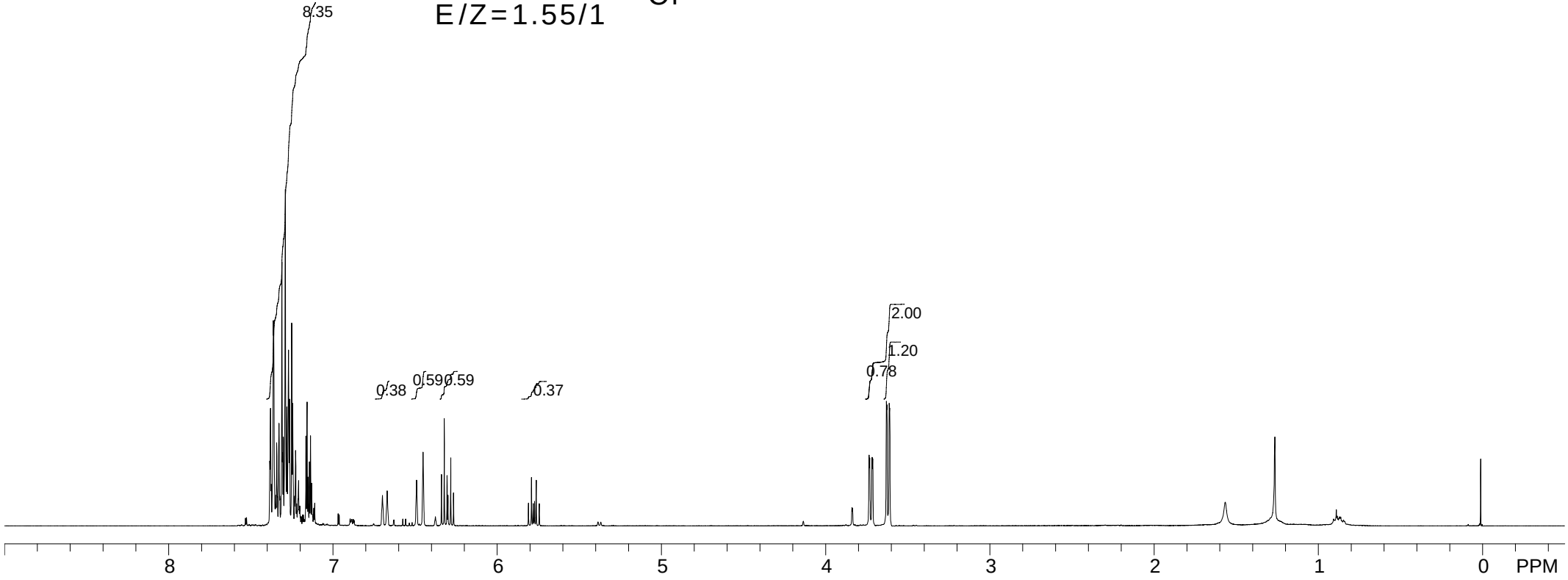
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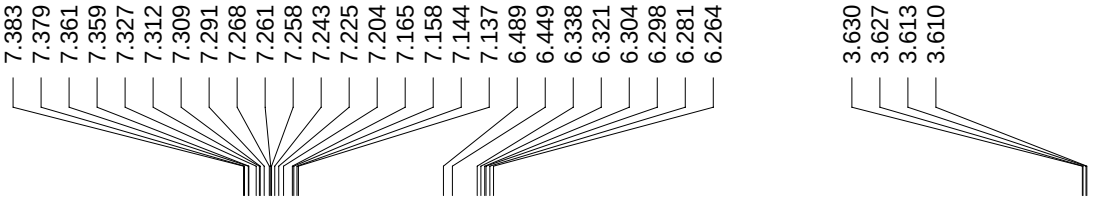
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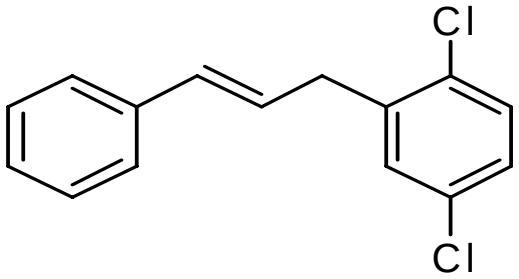
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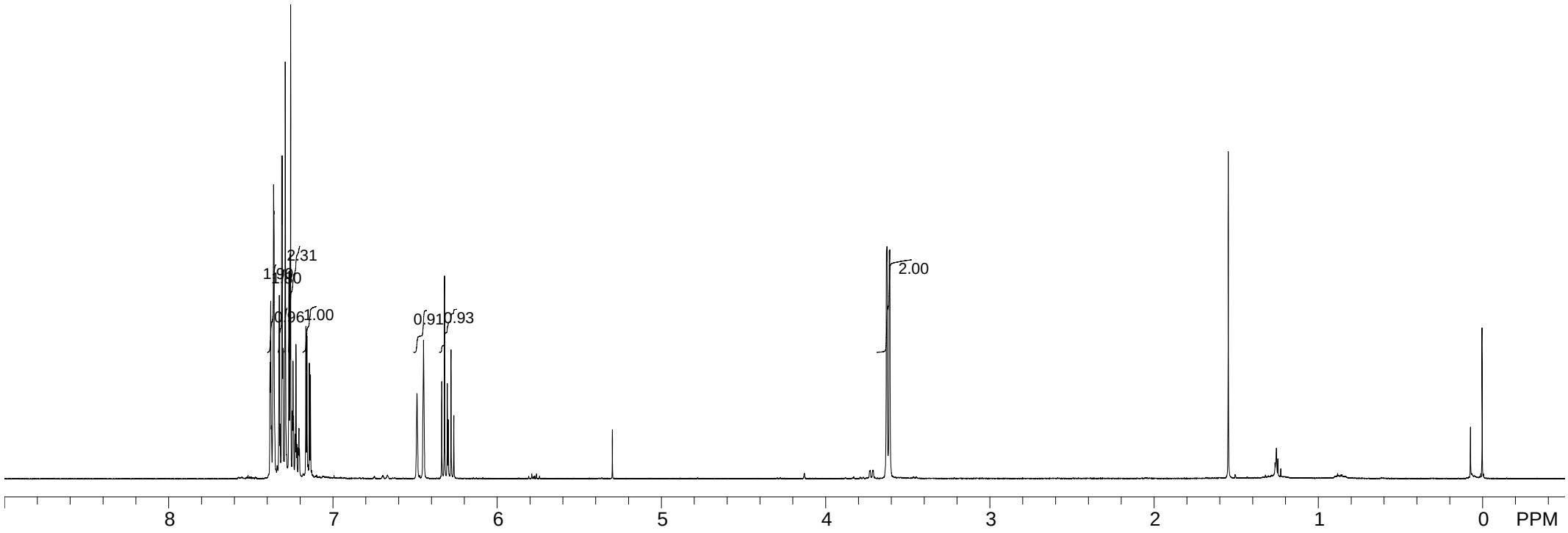
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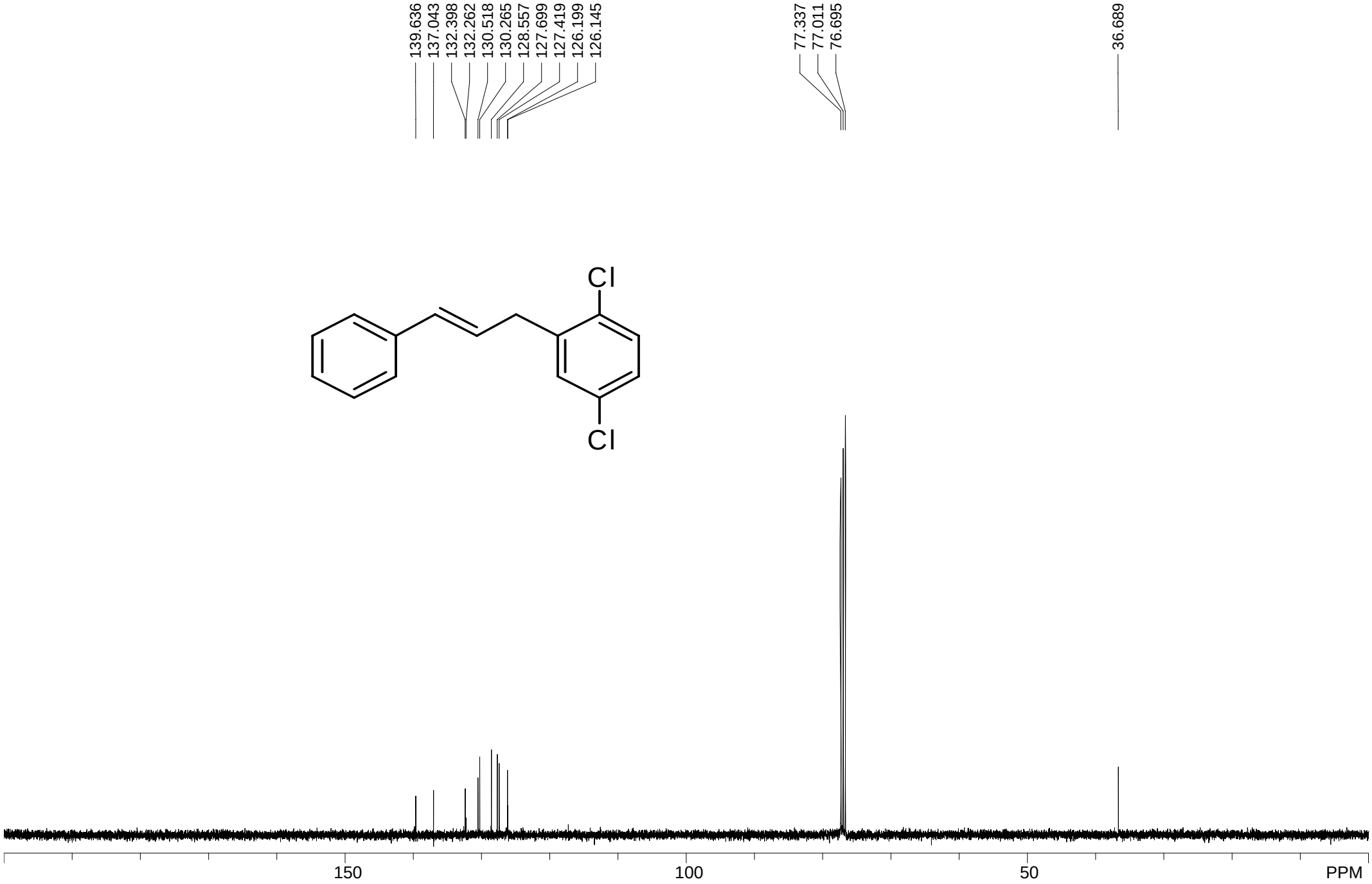
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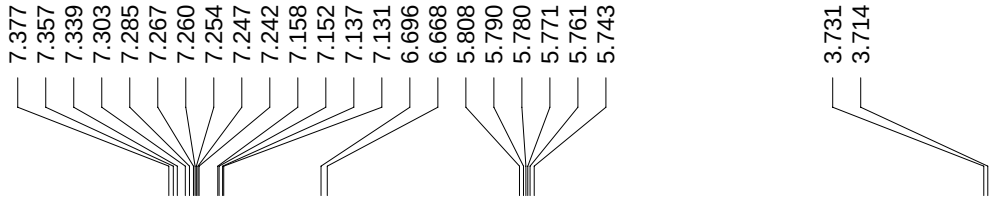
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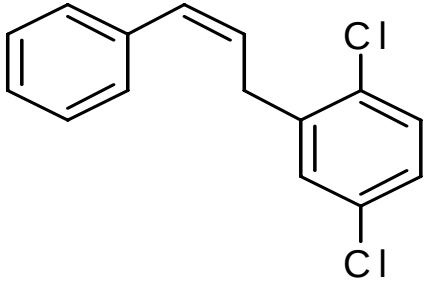
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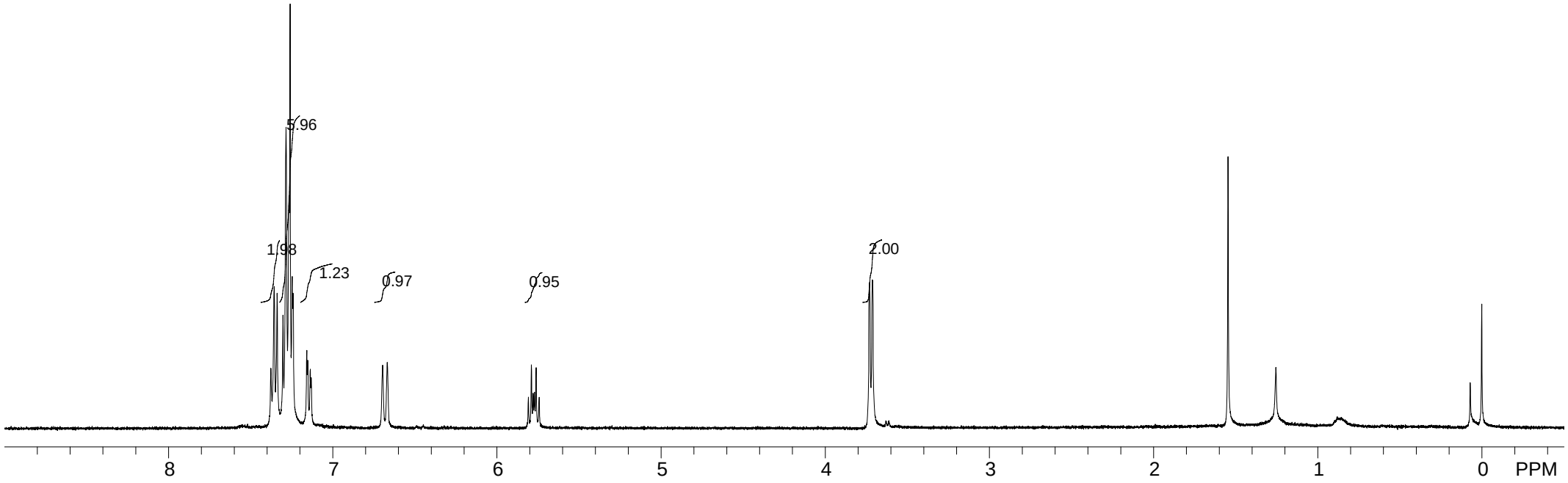
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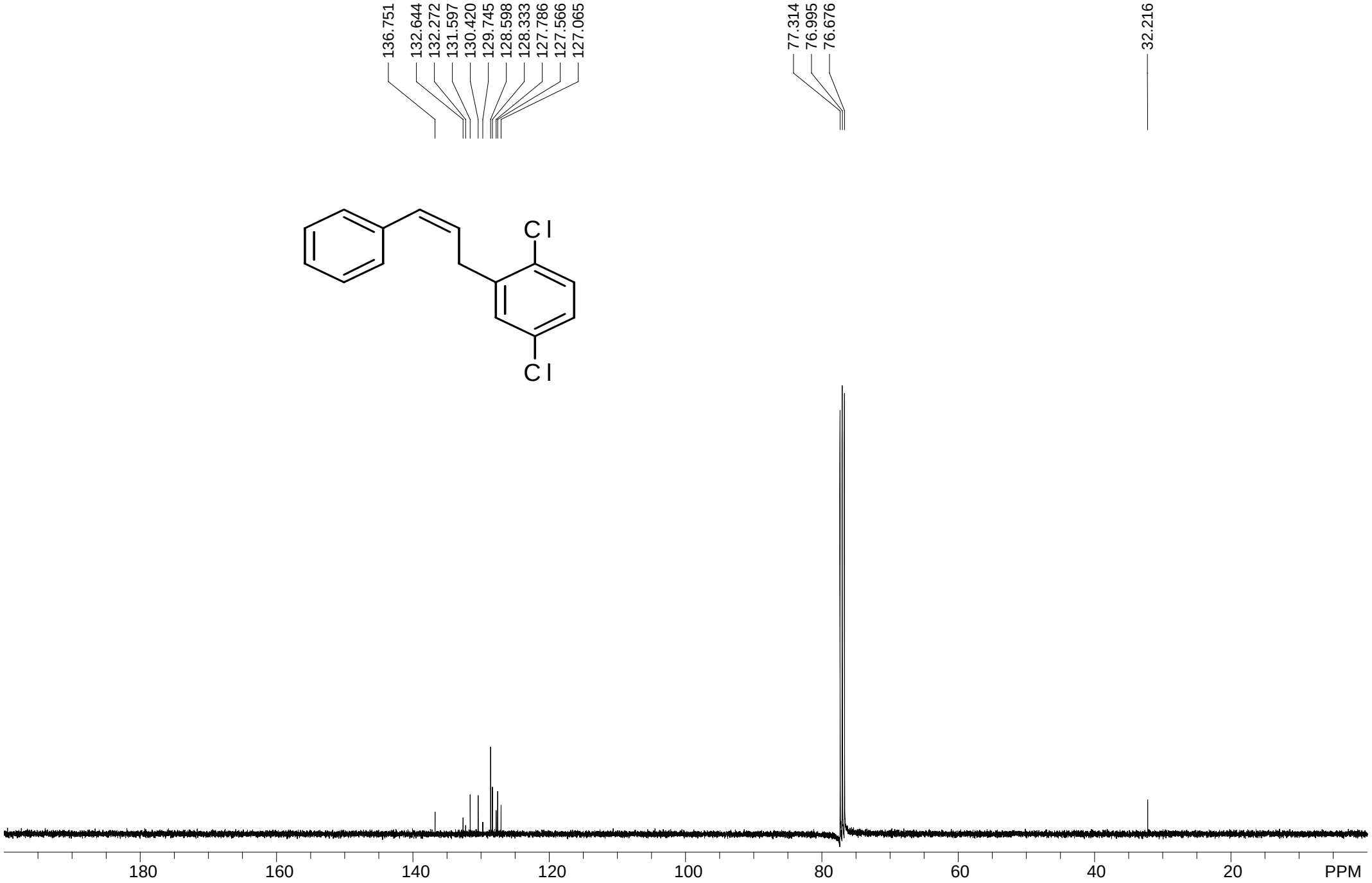
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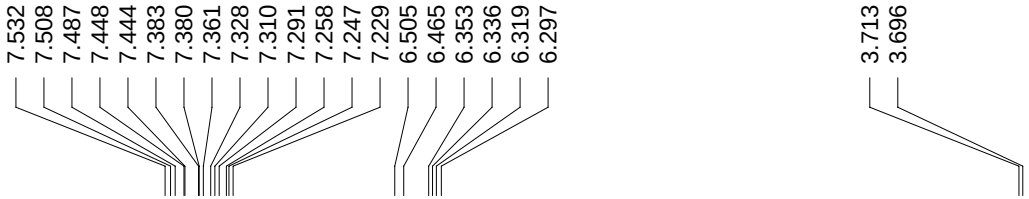
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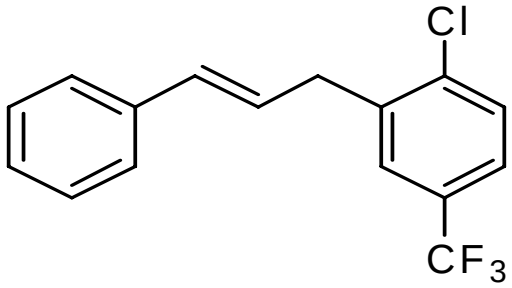
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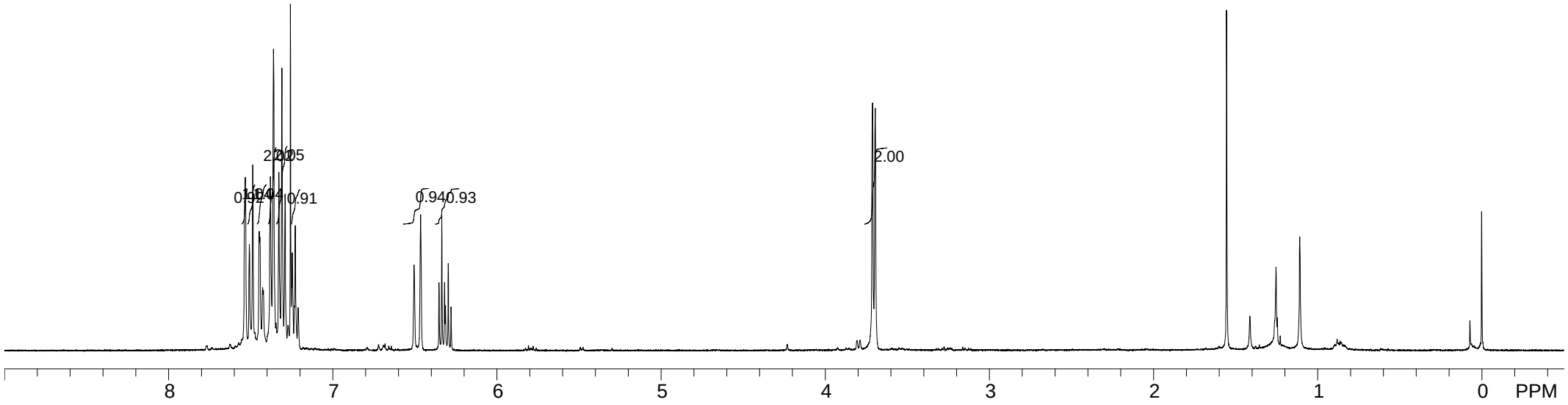
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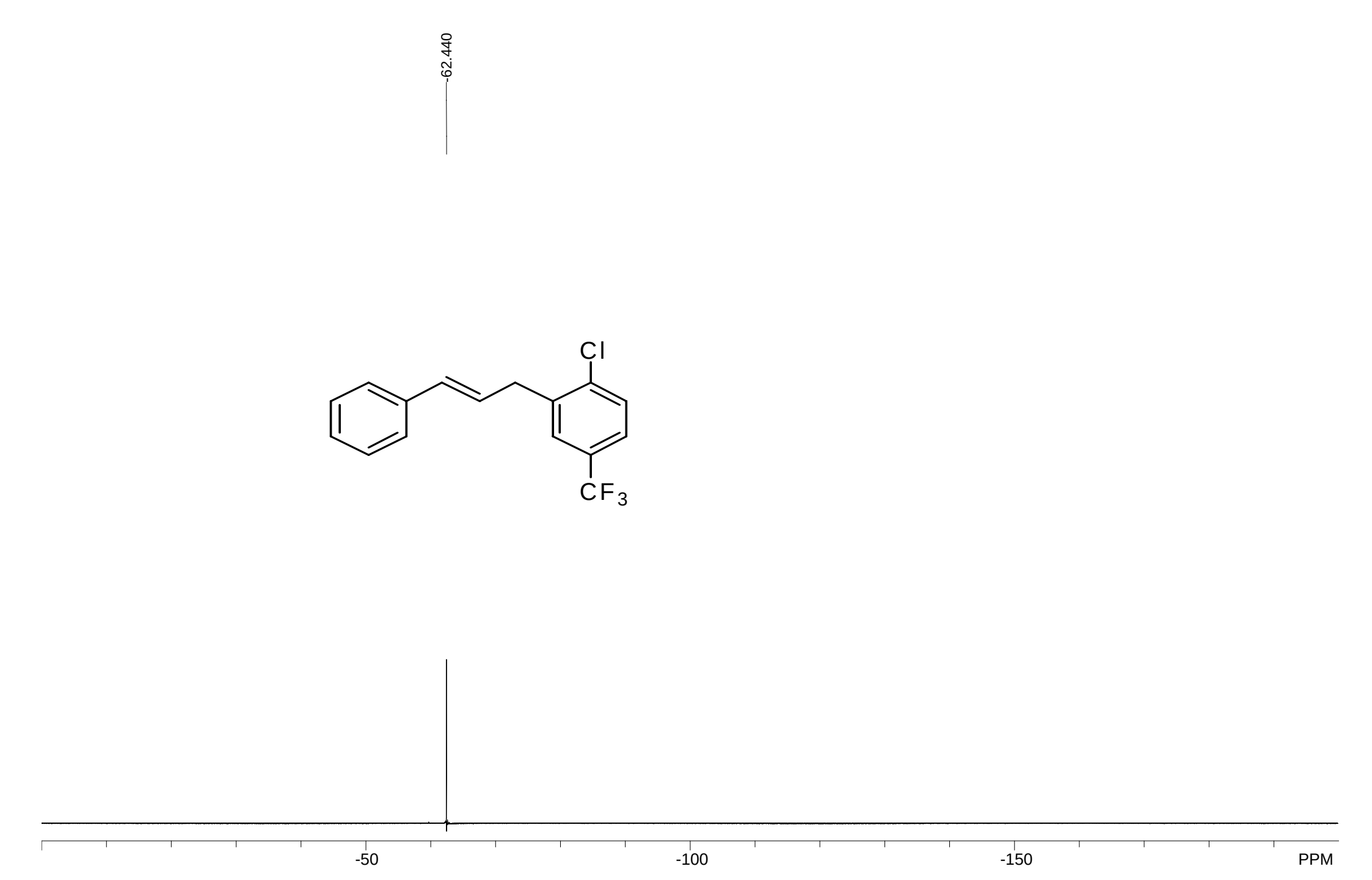
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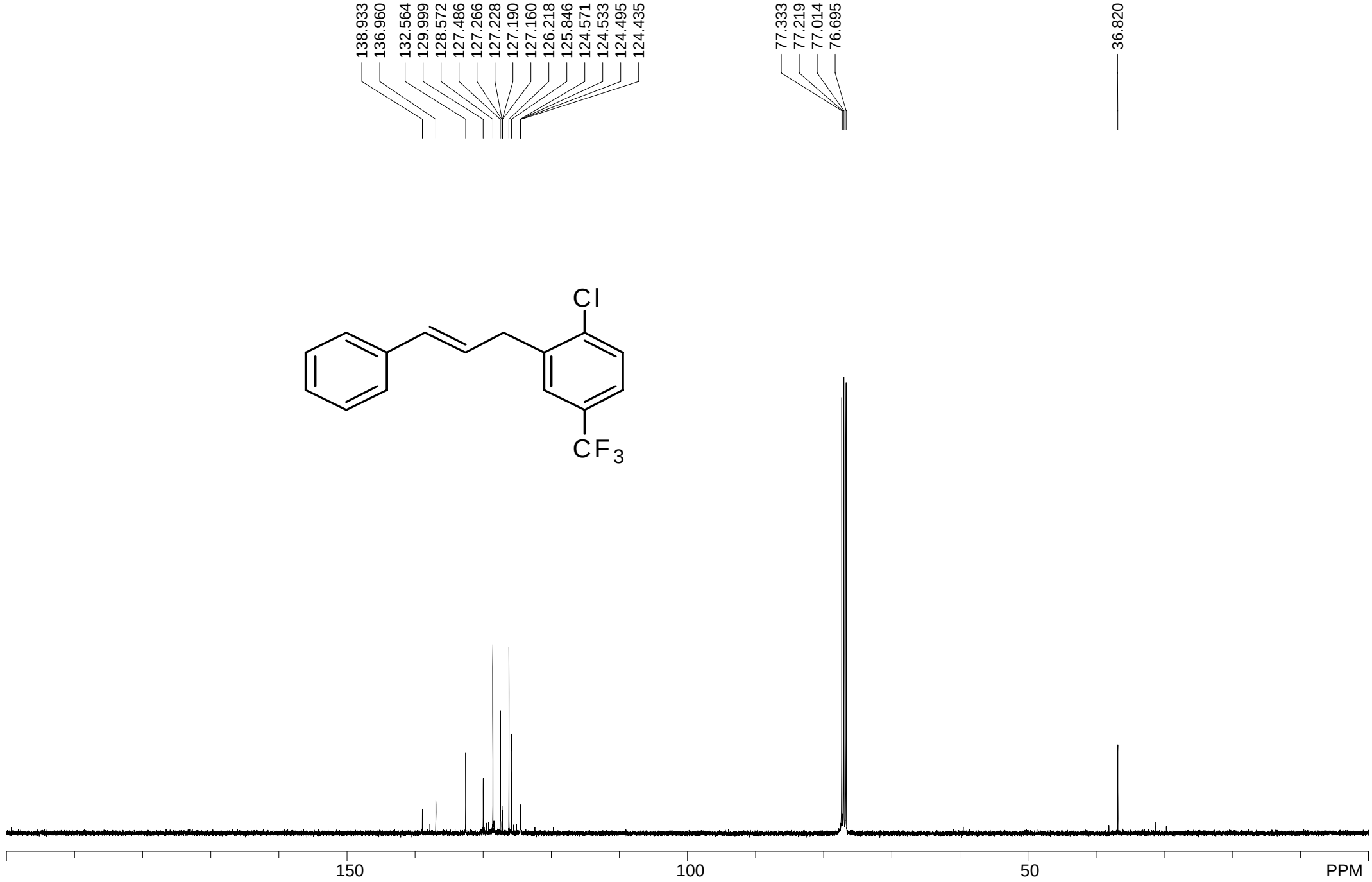
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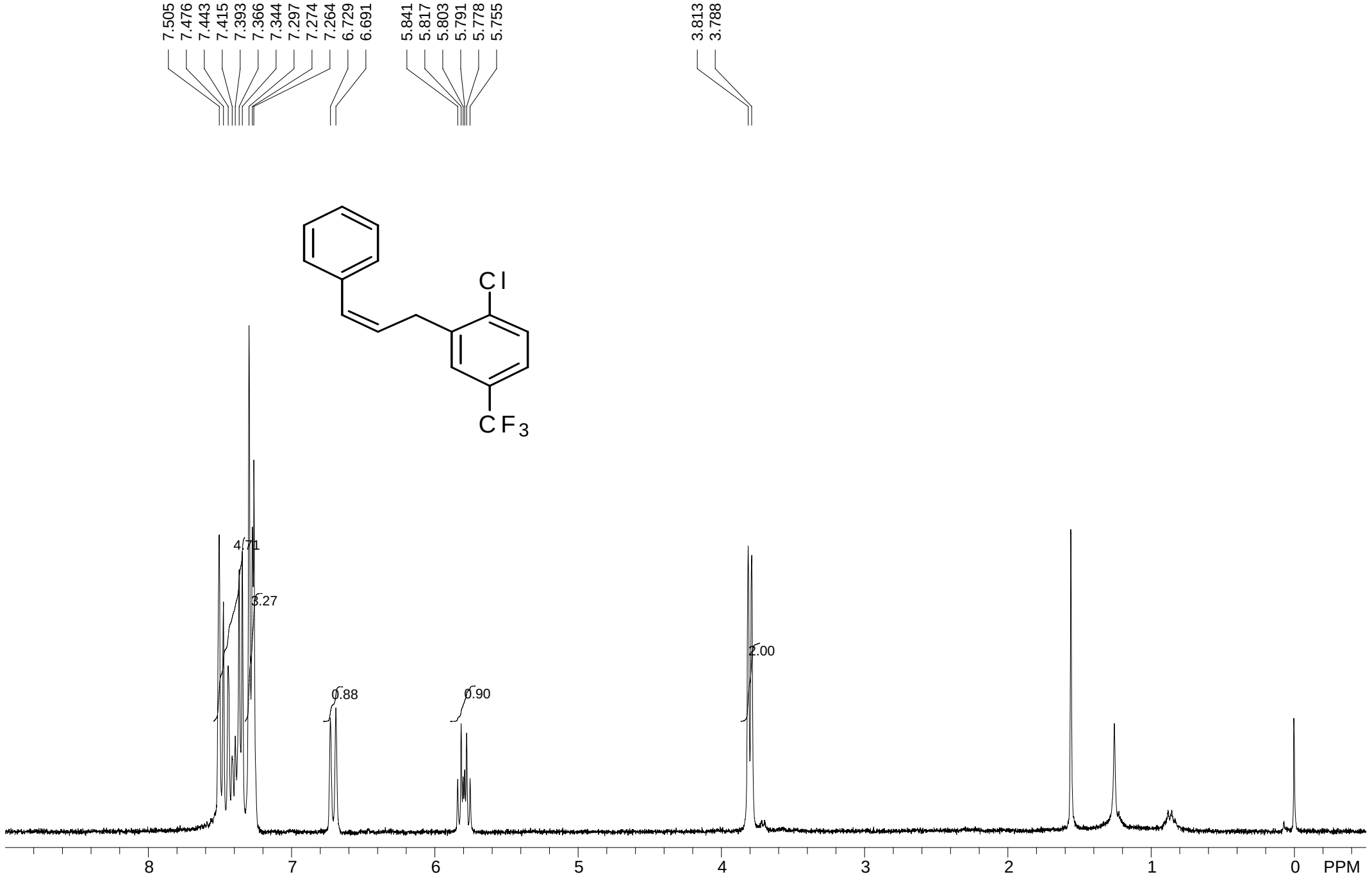
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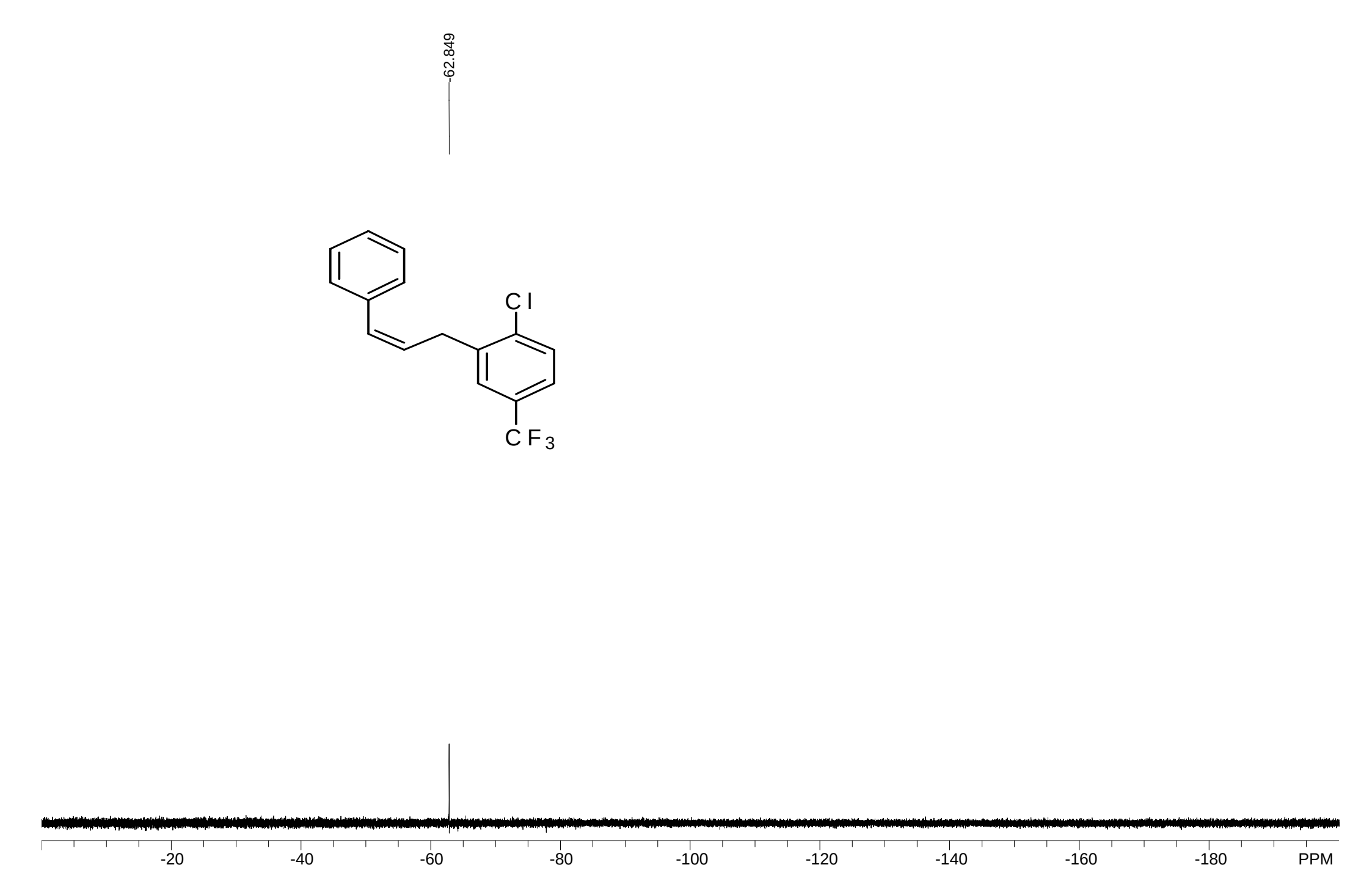
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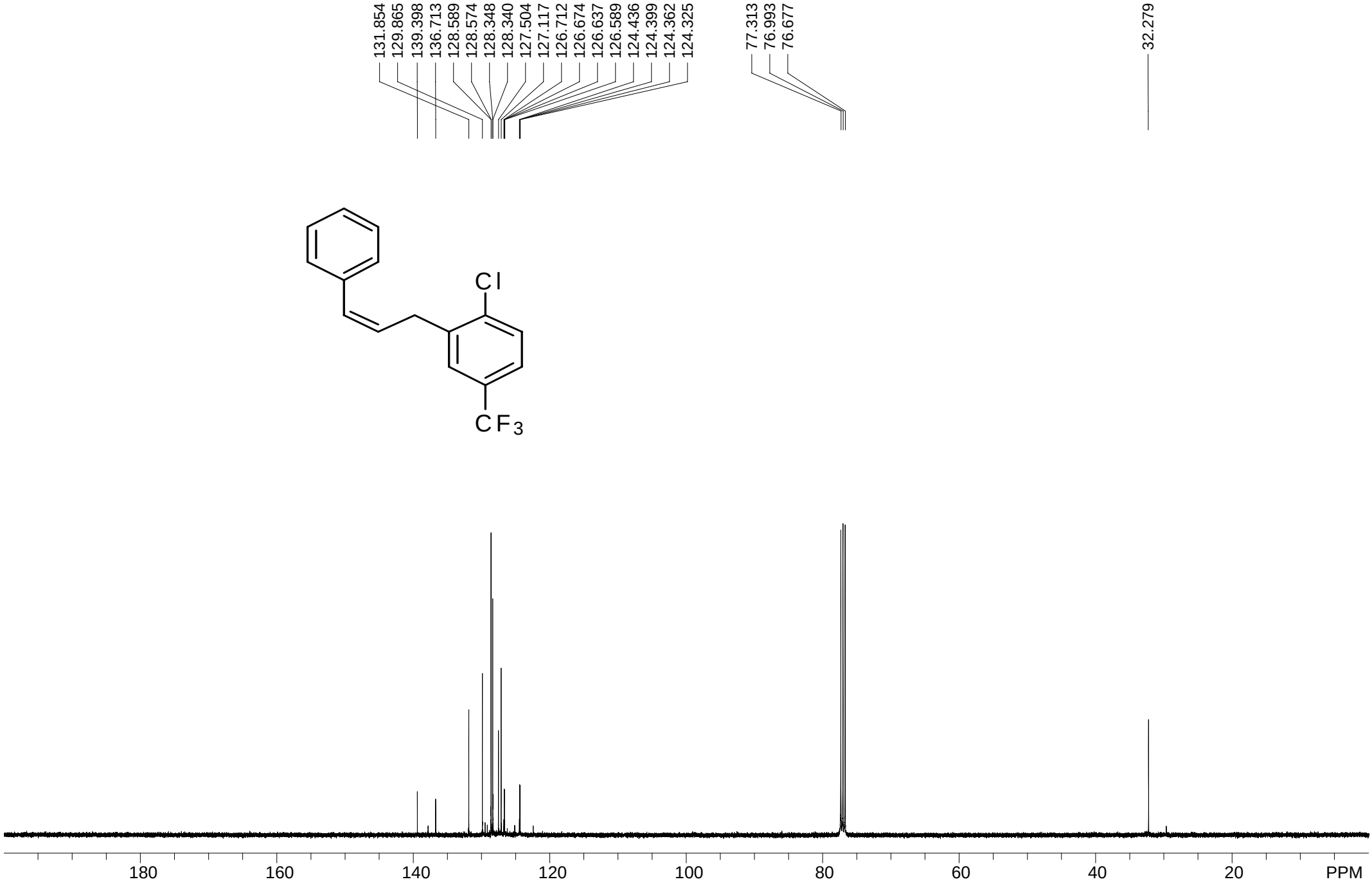
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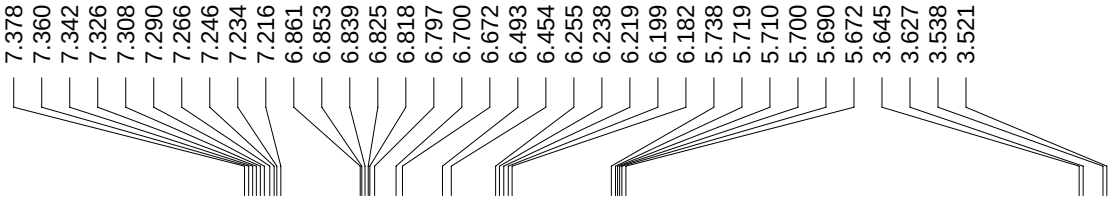
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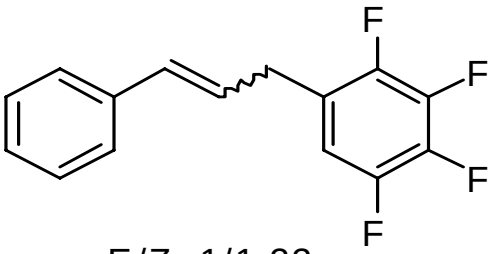
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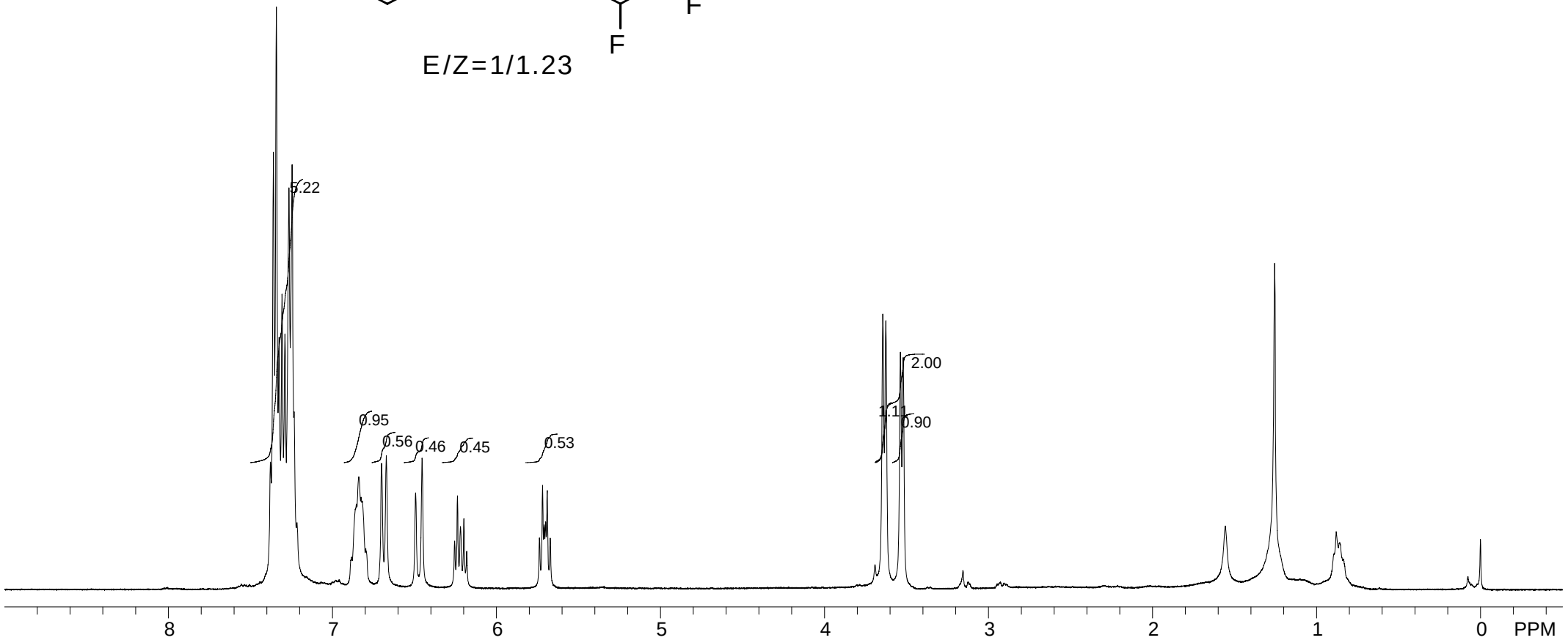
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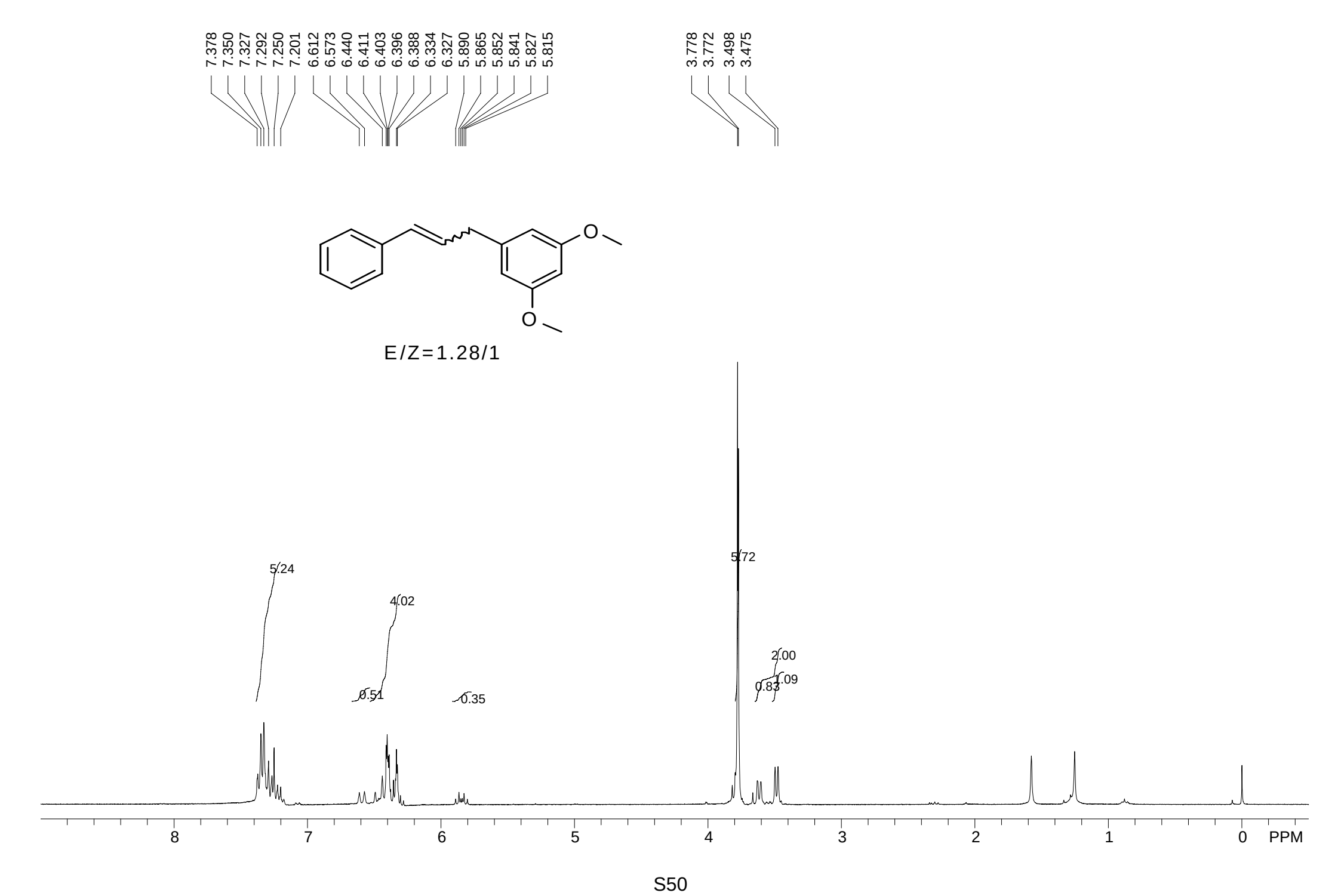
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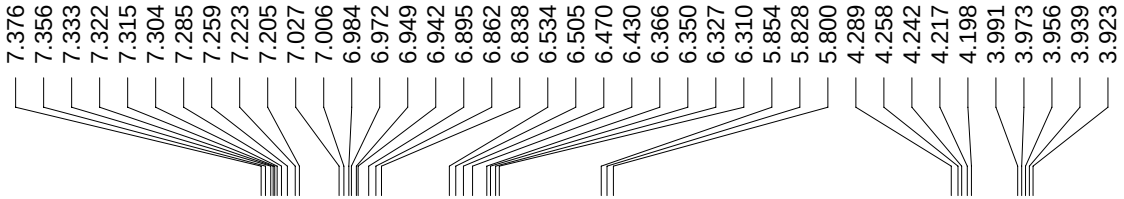
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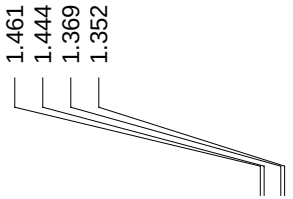
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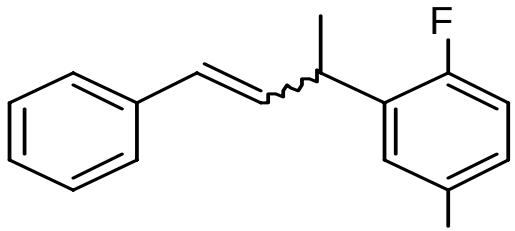
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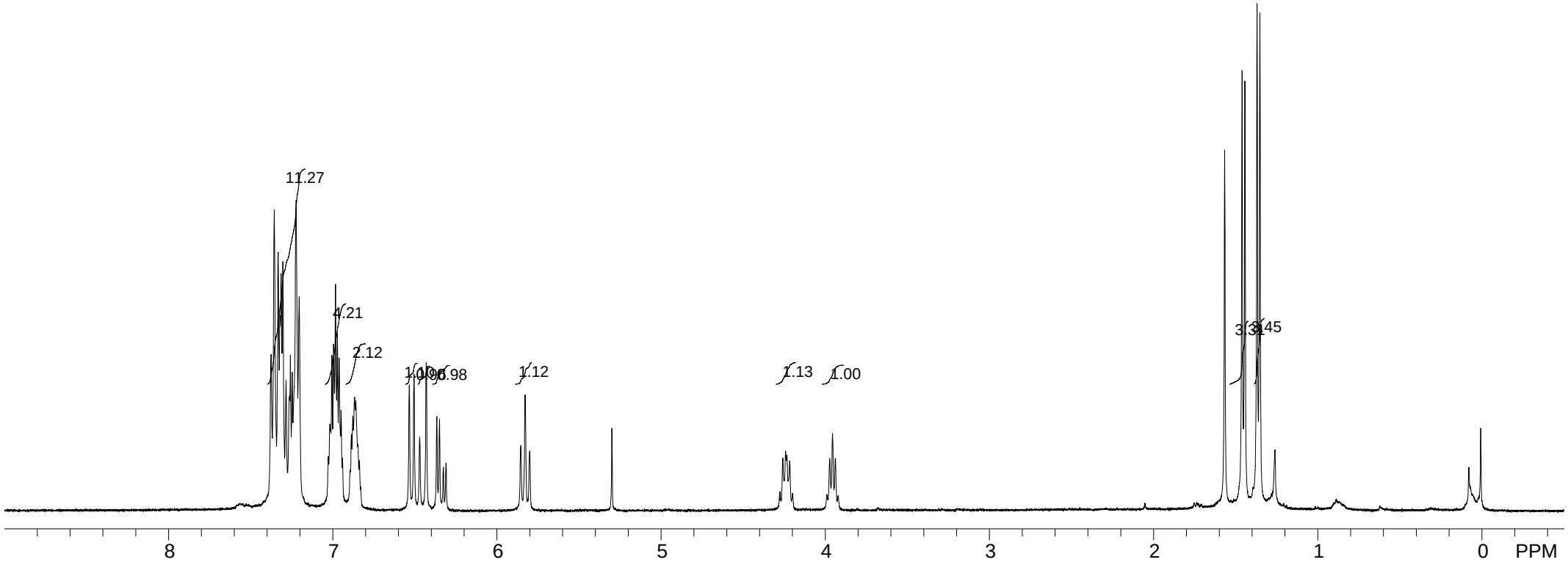
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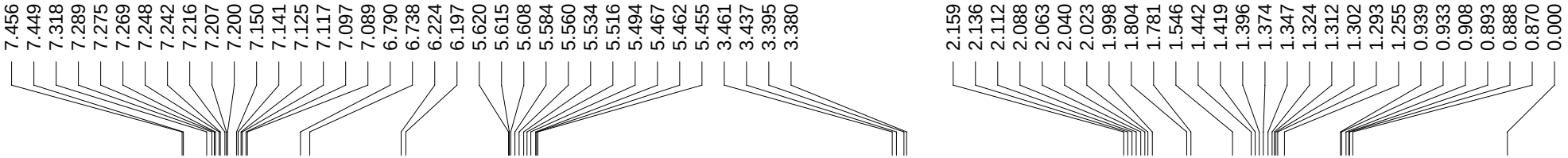
2.12
1.06
1.06
0.98
1.12
1.13
1.00
3.45
8
7
6
5
4
3
2
1
0
PPM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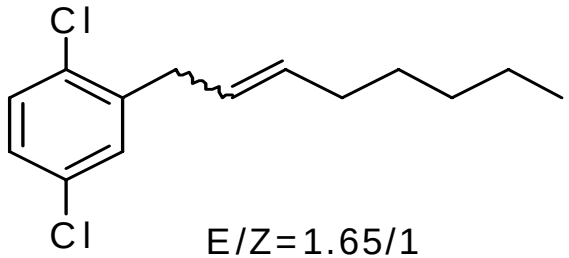
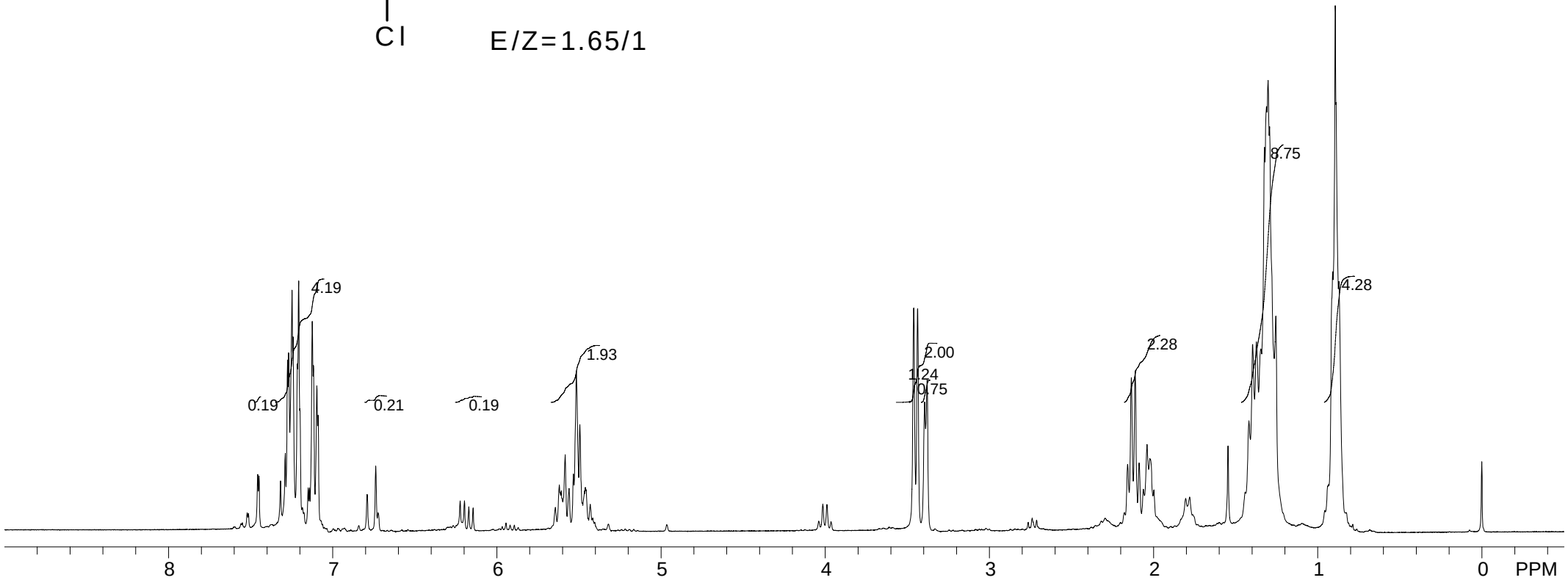
7.242
7.216
7.207
7.200
7.150
7.141
7.125
7.117
7.097
7.089
6.790
6.738
6.224
6.197
5.620
5.615
5.608
5.584
5.560
5.534
5.516
5.494
5.467
5.462
5.455
3.461
3.437
3.395
3.380
2.159
2.136
2.112
2.088
2.063
2.040
2.023
1.998
1.804
1.781
1.546
1.442
1.419
1.396
1.374
1.347
1.324
1.312
1.302
1.293
1.255
0.939
0.933
0.908
0.893
0.888
0.870
0.000


Cl
Cl

E/Z=1.65/1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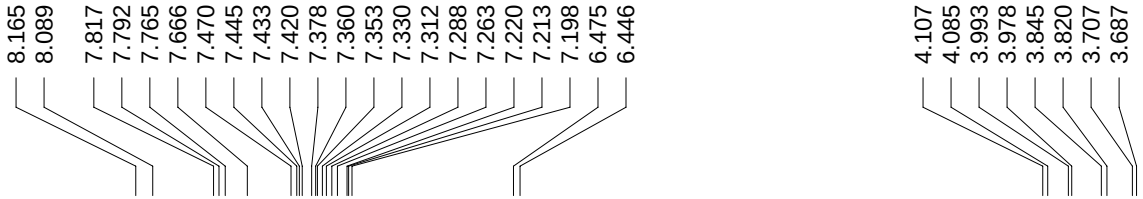
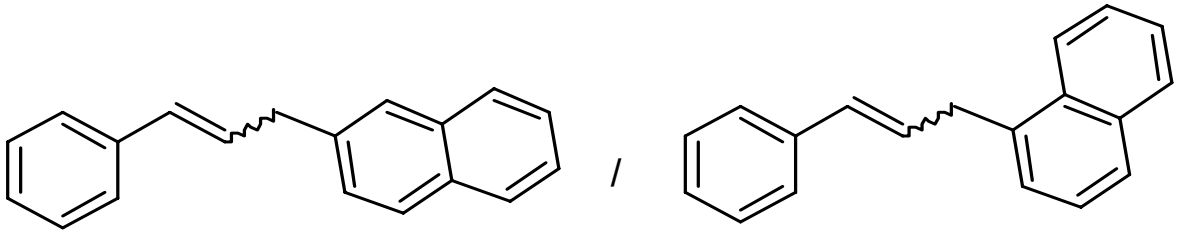
0.21
0.19
1.93
2.00
1.24
0.75
2.28
8.75
4.28
8
7
6
5
4
3
2
1
0
PPM





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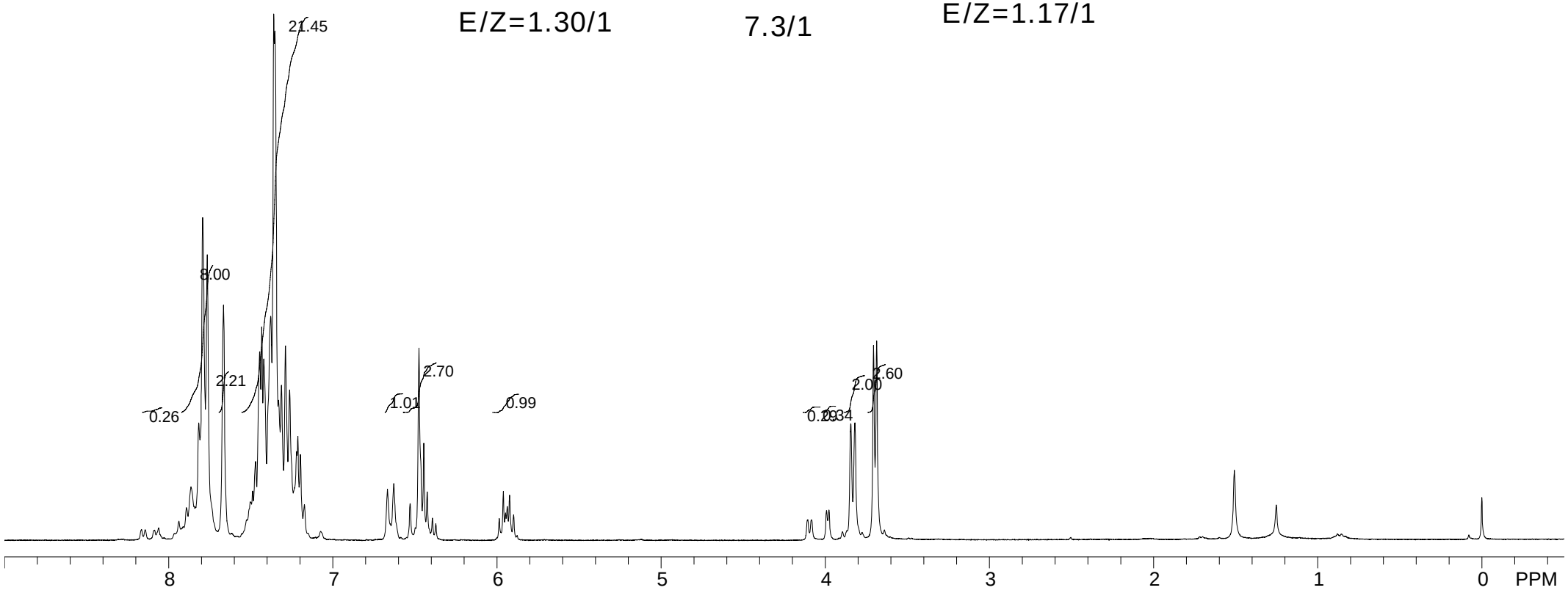

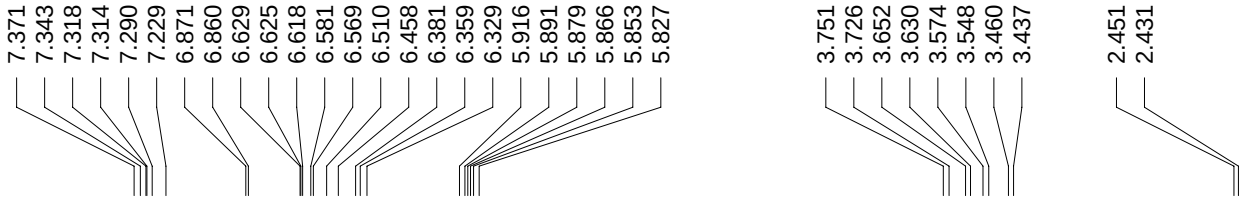

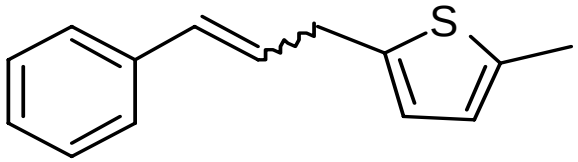

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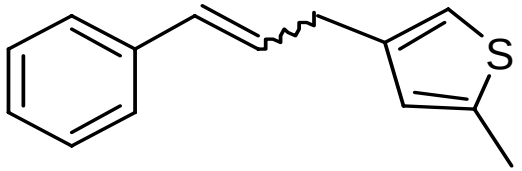

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7.4/1